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Contents

Some aspects of the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$ . . . . . . Julian R. Goldsmith 471
The Moore County meteorite: A further study with comment on its primordial environment . . . . H. H. Hess and E. P. Henderson 494
Atterberg plastic limits of clay minerals . . . . W. Arthur White 508
The dufrenite problem . . . . Clifford Frondel 513
Frondelite and the frondelite-rockbridgeite series . . . . . Marie Louise Lindberg 541
Variations in differential thermal analysis curves of siderite . . . . Richards A. Rowland and Edward C. Jonas 550
Muscovite with small optic axial angle . . . . . . J. M. Axelrod and F. S. Grimaldi 559
Paragenesis of the garnet and associated minerals of the Barton Mine near North Creek, New York . . . . B. M. Shaub 573
The laboratory growth of quartz . . . . I. I. Friedman 583
X-ray study of holdenite, mooreite and torreyite . . . . Joan Prewitt-Hopkins 589
Quartz sphere grown into a faced crystal . . . . Danforth R. Hale and Cornelius S. Hurlbut, Jr. 596
Notes and news: Some notes on the point counter . . . . F. Chayes 600
A note on the conversion of amorphous silica to quartz . . . . Donald A. Bailey 601
An improved method of etching iron meteorites . . . . B. O. Reberholt and E. P. Henderson 606
Bodenbenderite, a discredited species . . . . Charles Milton and Alfred Tennyson Myers 608
Corrections to recent papers on probertite and lindgrenite . . . . William H. Barnes 611
Proceedings of societies: Mineralogical Society (London) 614
Book reviews 616
New mineral names 618

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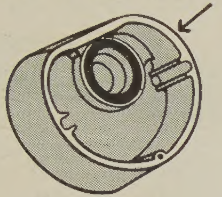

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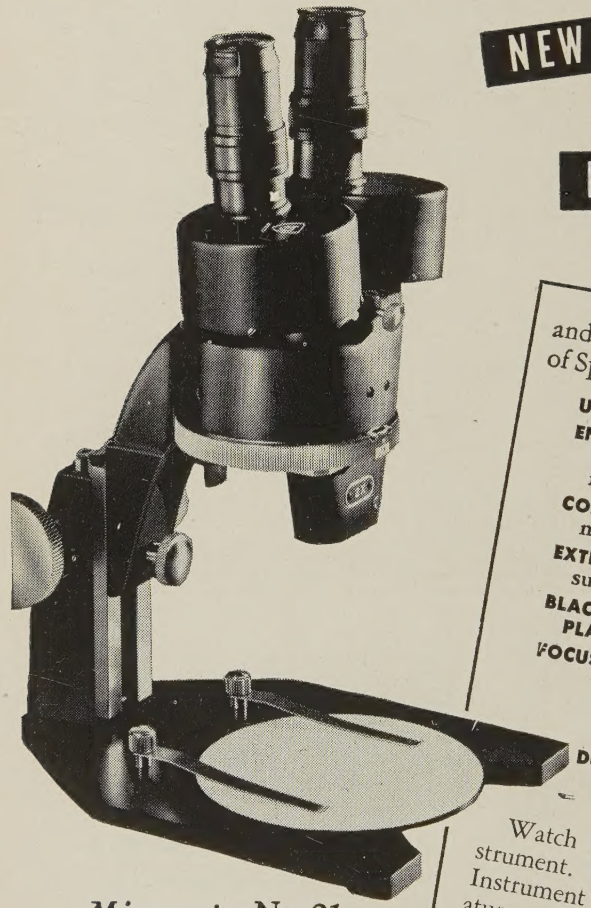

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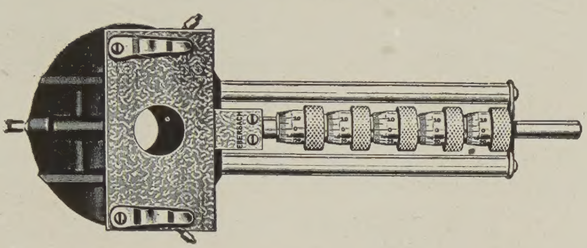

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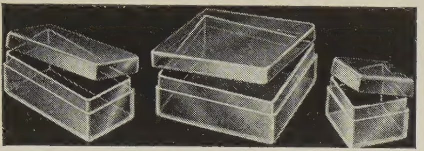

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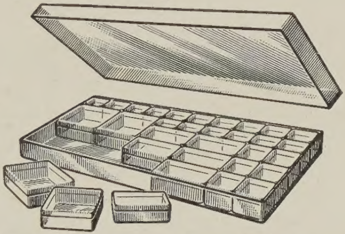

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SOME ASPECTS OF THE SYSTEM $NaAlSiO_4$–$CaO \cdot Al_2O_3$

JULIAN R. GOLDSMITH, *University of Chicago, Chicago, Illinois.*

ABSTRACT

The thermal-equilibrium relationships in the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$ have been investigated. Complex relations exist at temperatures above the carnegieite-nepheline inversion range, the system at these temperatures being quaternary in nature. At lower temperatures, in the stability field of nepheline, simplification to a binary system is observed over a considerable portion of the system due to the ability of nepheline to take up somewhat over 60 per cent $CaO \cdot Al_2O_3$ in solid solution. The complexity at higher temperatures is due to the inability of carnegieite to include more than a small amount of $CaO \cdot Al_2O_3$ in its structure, and to the intrusion of fields of β-Al_2O_3, corundum, and $CaO \cdot 2\ Al_2O_3$.

Soda volatilization is significant in the system, and apparently the rate is increased as lime is added. As soda is lost, β-Al_2O_3 or corundum tends to crystallize. The possibility of this effect being related to the corundum present in some alkaline rocks, particularly those associated with limestone, and to soda enrichment (albitization, etc.) of the country rock is discussed.

I. INTRODUCTION

Investigations in the quaternary system Na_2O-CaO-Al_2O_3-SiO_2 have been confined for the most part to compositions fairly rich in silica. If this four component system be represented as a tetrahedron, it is seen that the synthetic counterparts of silicate minerals naturally occur toward the silica corner of the tetrahedron, and the equilibrium relations between these minerals are of primary interest to the petrologist. In a previous work by the author (1947) on the system anorthite-gehlenite-nepheline, it was noted that the high refractive indices of some of the nepheline crystals encountered presented a compositional problem not satisfied by assuming solid solution with any "end-member molecules" present in the system. Non-ternary behavior of crystallization paths also contributed to the conclusion that the hitherto recognized solid solutions of albite and anorthite (not considering $KAlSiO_4$) in nepheline could not account for the nepheline formed in this system. Higher indices than those previously observed in synthetic nepheline had also been noted by Smalley (1947), in his study of the system nepheline-gehlenite.

Consideration of courses of crystallization within the three dimensional tetrahedron Na_2O-CaO-Al_2O_3-SiO_2 led the writer (1947) to the conclusion that at least part of the material entering into solid solution with nepheline in the system anorthite-gehlenite-nepheline was alumina-rich in composition; i.e., the nephelines were undersilicated. A. N. Winchell (1933) had suggested the possibility that the lime observed in natural nephelines might be present as $CaAlAlO_4$. This calcium aluminate would satisfy the requirements discussed above, and was considered at that time, in addition to a sodium aluminate, $Na_2Al_2O_4$. $CaAlAlO_4$ is known as an independent crystalline compound, and is commonly written as $CaO \cdot Al_2O_3$. If one assumes solid solution between it and nepheline,

$$\begin{matrix} NaAlSiO_4 \\ CaAlAlO_4 \end{matrix}$$

it is apparent that the common Na-Ca and Al-Si replacement would be operative. The present investigation was begun primarily to determine the validity of this relationship.

The thermal-equilibrium relationships at atmospheric pressure along the join $NaAlSiO_4$-$CaO \cdot Al_2O_3$ within the parent four oxide system are here discussed. The relation of this join to the general quaternary system is shown in Fig. 1. One of the end members, $NaAlSiO_4$ is the principal "molecule" of natural nepheline, whereas the compound $CaO \cdot Al_2O_3$ is not known to occur independently in nature. $NaAlSiO_4$ is a polymorphic compound; carnegieite, the high temperature modification is also known only as a synthetic product. The compound $CaO \cdot Al_2O_3$, although an end member in the system, does not crystallize in those portions of the system here investigated (from zero to 80% $CaO \cdot Al_2O_3$). A calcium aluminate phase is encountered, but in all cases it is the 1:2 compound ($CaO \cdot 2Al_2O_3$) rather than the 1:1 compound. This phenomenon will later be discussed in the light of relations within the general four oxide system.

The crystalline phases encountered in this system are nepheline (solid solutions), carnegieite (solid solutions), β-Al_2O_3, corundum, and $CaO \cdot 2Al_2O_3$. The compound $CaO \cdot Al_2O_3$ would undoubtedly form in mixtures very rich in this ingredient. Nine mixtures were prepared and subjected to thermal study. In addition, a few thermal and x-ray determinations were made on the three phases of pure $NaAlSiO_4$,[1] and pure $CaO \cdot Al_2O_3$ was prepared for optical and x-ray examination. Thermal study was by the quenching method in all cases that involved a liquid phase. In runs below solidus temperatures the small charges, in platinum-foil envelopes, were rapidly cooled in air. The resulting products were examined microscopically, and in many cases, also by means of x-ray diffraction (powder pictures). Approximately 170 runs were made, the sig-

[1] Kindly supplied as glass, carnegieite, and nepheline by Dr. N. L. Bowen, of the Geophysical Laboratory, Carnegie Institution of Washington.

nificant data of which are summarized in Table 1. The equilibrium diagram, Fig. 2, was prepared from these data. Figure 3 is a composition-refractive index diagram of the homogeneous glasses prepared along the join studied.

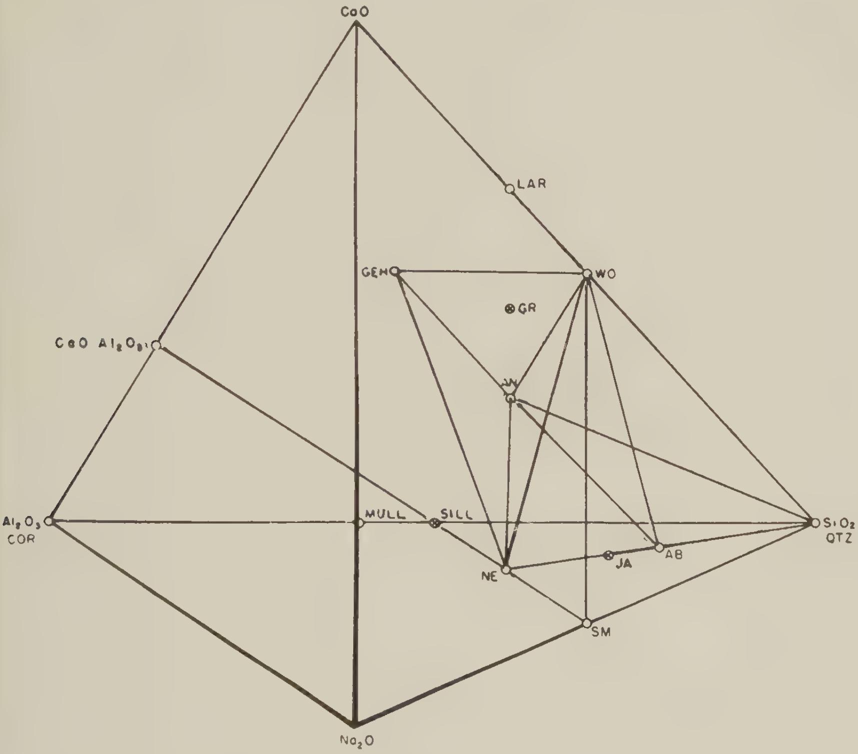

FIG. 1. The soda-lime-alumina-silica tetrahedron. The join here studied is represented by the line between NE and $CaO \cdot Al_2O_3$. Other internal systems that have been investigated are shown by lines joining the composition points. The compounds that have been prepared synthetically are shown as ○; those that occur in nature but that have not been synthesized are shown thus: ⊗.

The abbreviations signify; AN, anorthite; GEH, gehlenite; NE, nepheline; WO, wollastonite; AB, albite; JA, jadeite; SM, sodium metasilicate; SILL, sillimanite; MULL, mullite; LAR, larnite; GR, grossularite; QTZ, quartz; COR, corundum.

II. THE CRYSTALLINE PHASES

$NaAlSiO_4$

The properties of carnegieite, the high temperature modification of $NaAlSiO_4$, and of nepheline, the low temperature form, have been described by Bowen (1912), and by Bowen and Greig (1925). Carnegieite

TABLE 1. THERMAL DATA FOR THE SYSTEM $NaAlSiO_4$-$CaO \cdot Al_2O_3$

Wt. per cent		Time	Temperature (° C.)	Final Condition*
$NaAlSiO_4$-	$CaO \cdot Al_2O_3$			
95	5	3½ hrs.	1344	CG, thin films of glass
		3¼ hrs.	1340	CG, NE
		90 hrs.	1060	NE, CG
		15 days	795	CG, NE
90	10	30 min.	1488	All glass
		30 min.	1484	Glass, CG
		4 hrs.	1345	CG, glass, rare β-Al_2O_3
		4 hrs.	1350	CG, glass
		20 hrs.	1336	CG, glass, β-Al_2O_3
		5½ hrs.	1330	CG, NE, β-Al_2O_3
		22 hrs.	1306	NE, CG, very rare β-Al_2O_3
		20 hrs.	1300	NE, CG
		10 days	795	NE, CG
80	20	30 min.	1440	All glass
		30 min.	1437	Glass, rare CG
		3¾ hrs.	1368	CG, glass
		3¾ hrs.	1362	CG, glass, rare β-Al_2O_3
		3¾ hrs.	1336	CG, β-Al_2O_3, sparse glass
		3¾ hrs.	1331	CG, β-Al_2O_3, NE (some glass?)
		3½ hrs.	1323	CG, NE, rare β-Al_2O_3
		3½ hrs.	1317	CG, NE
		10 days	795	NE, CG
70	30	30 min.	1398	All glass
		30 min.	1394	Glass, sparse CG
		30 min.	1384	Glass, CG
		30 min.	1380	Glass, CG, rare β-Al_2O_3
		3½ hrs.	1390	Glass, fairly abundant β-Al_2O_3†
		3½ hrs.	1340	CG, β-Al_2O_3, glass
		3½ hrs.	1335	NE, CG, β-Al_2O_3
		3½ hrs.	1325	NE, CG, β-Al_2O_3
		3½ hrs.	1319	NE, CG
		10 days	795	NE, CG

* CG = Carnegieite SS
NE = Nepheline SS
1:2 cpd. = $CaO \cdot 2Al_2O_3$
cor. = corundum

† Here is seen effect of Na_2O volatilization. A longer run shows β-Al_2O_3 in place of CG. (Compare with run at 1394° for 30 minutes.)

TABLE 1—(*continued*)

Wt. per cent		Time	Temperature (° C.)	Final Condition*
$NaAlSiO_4$	$CaO \cdot Al_2O_3$			
65	35	30 min.	1410	All glass
		30 min.	1406	Glass, rare β-Al_2O_3
		30 min.	1374	Glass, β-Al_2O_3
		30 min.	1370	Glass, β-Al_2O_3, rare CG
60	40	30 min.	1423	All glass
		30 min.	1419	Glass, rare β-Al_2O_3
		30 min.	1356	Glass, β-Al_2O_3
		30 min.	1352	Glass, β-Al_2O_3, rare CG
		30 min.	1348	Glass, β-Al_2O_3, sparse CG, rare 1:2 cpd
		45 min.	1340	NE, CG, sparse glass, β-Al_2O_3
		3 hrs.	1336	NE, CG, β-Al_2O_3
		4 hrs.	1315	NE, CG, rare β-Al_2O_3
		3 hrs.	1305	NE, CG
		10 days	795	NE, rather sparse CG
50	50	30 min.	1457	All glass
		30 min.	1453	Glass, rare 1:2 cpd.
		30 min.	1437	Glass, 1:2 cpd.
		30 min.	1433	Glass, 1:2 cpd, very rare cor.
		45 min.	1356	1:2 cpd, glass, rather rare cor.
		45 min.	1352	1:2 cpd, glass, rare CG, rather rare cor.
		3½ hrs.	1348	1:2 cpd, glass, rare CG, rare cor.
		2½ hrs.	1344	1:2 cpd, NE, CG, glass
		3½ hrs.	1335	NE, CG, sparse 1:2 cpd, rare glass
		3½ hrs.	1331	NE, CG, very rare 1:2 cpd., very rare β-Al_2O_3
		24 hrs.	1322	NE, sparse CG, sparse 1:2 cpd., rare β-Al_2O_3
		3 hrs.	1310	NE, sparse CG, sparse 1:2 cpd. (?)
		5 days	795	Glass, CG, NE
		25 days	795	NE, sparse CG
40	60	30 min.	1507	All glass
		30 min.	1503	Glass, sparse 1:2 cpd.
		30 min.	1462	1:2 cpd., glass
		30 min.	1458	1:2 cpd., glass, rare cor.
		45 min.	1370	1:2 cpd., glass, cor.
		45 min.	1366	1:2 cpd., glass, cor., rare CG
		1½ hrs.	1352	1:2 cpd., glass, sparse CG, cor. (?)
		1½ hrs.	1347	1:2 cpd., glass, CG, NE
		3½ hrs.	1334	NE, 1:2 cpd., CG, rare glass
		3½ hrs.	1330	NE, 1:2 cpd., CG (rare cor. ?)

TABLE 1—(*continued*)

Wt. per cent		Time	Temperature (° C.)	Final Condition*
$NaAlSiO_4$	$CaO \cdot Al_2O_3$			
40	60	24 hrs.	1322	NE, rather sparse 1:2 cpd., sparse CG (rare β-Al_2O_3 ?)
		3½ hrs.	1310	NE, sparse CG, small high index inclusions (1:2 cpd. ?)
		5 days	795	Glass, sparse CG
		25 days	795	NE, CG, sparse glass
		46 days	795–900	NE, moderate CG
20	80	1½ hrs.	1444	1:2 cpd., glass
		1½ hrs.	1440	1:2 cpd., glass, cor.
		2½ hrs.	1387	1:2 cpd., cor., rare CG, rare glass

melts at 1526° C., is isometric up to its melting point, but inverts to a triclinic form below 690° C. A second inversion, accompanied by a marked change in birefringence, occurs at 226.5° C. The indices of refraction of the low-temperature form are $\alpha = 1.514$, $\beta = 1.514$, $\gamma = 1.509$. Carnegieite typically occurs in globular masses showing no external crystal form, but with intricate twinning that forms as a result of inversion.

The carnegieite obtained in the present study is considerably altered by solid solution. Refractive indices as high as 1.535 were observed, and in mixes containing approximately 20 per cent or more $CaO \cdot Al_2O_3$, the high temperature isometric form becomes stabilized so that the low temperature inversions to the triclinic form do not take place during cooling. The carnegieite in these mixes appears under the microscope as a completely isotropic material, and if not characteristically globular, can be distinguished from glass that may be present only by difference in refractive index or by *x*-ray diffraction pattern. Smalley (1947) notes that carnegieite in the system $NaAlSiO_4$-$Ca_2Al_2SiO_7$ shows increasing refractive index and decreasing birefringence with added $Ca_2Al_2SiO_7$. He also states that glass (liquid) persists down to the lowest temperatures of observation throughout the system. It is probable that stabilized isometric carnegieite also was formed in the system studied by Smalley, and mistaken for glass.

Pure synthetic nepheline inverts to carnegieite at a temperature of 1254±5° C. (Greig and Barth, p. 108). Nepheline may take up to 35 per cent anorthite in solid solution, with a resulting rise in the inversion temperature of 100° C. (Bowen, 1912, p. 571). Albite also forms a solid solution with nepheline, raising the inversion temperature 30° at its

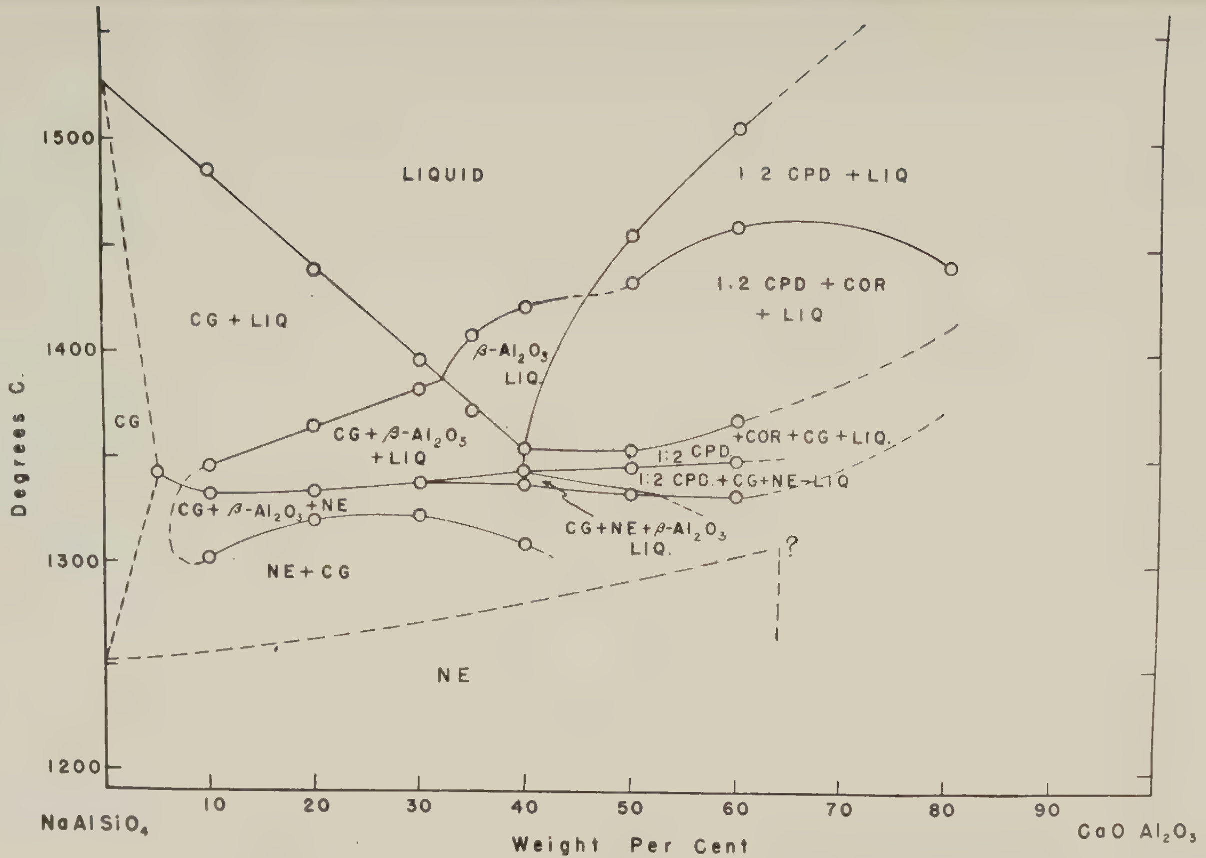

FIG. 2. Equilibrium diagram for the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$. NE and CG are solid solutions.

maximum concentration (Greig and Barth, p. 109). Smalley, in the system $NaAlSiO_4$-$Ca_2Al_2SiO_7$, found an inversion range extending from about 50° above, to 100° below the normal inversion point. The likelihood of the metastable existence of carnegieite below its stable inversion range will be later considered in more detail; it is possible that this could account for the apparently large interval observed by Smalley. The upper limit of the carnegieite-nepheline inversion observed in the present study varies between approximately 1330°–1350° C., a maximum increase of 100° C. over that in pure $NaAlSiO_4$.

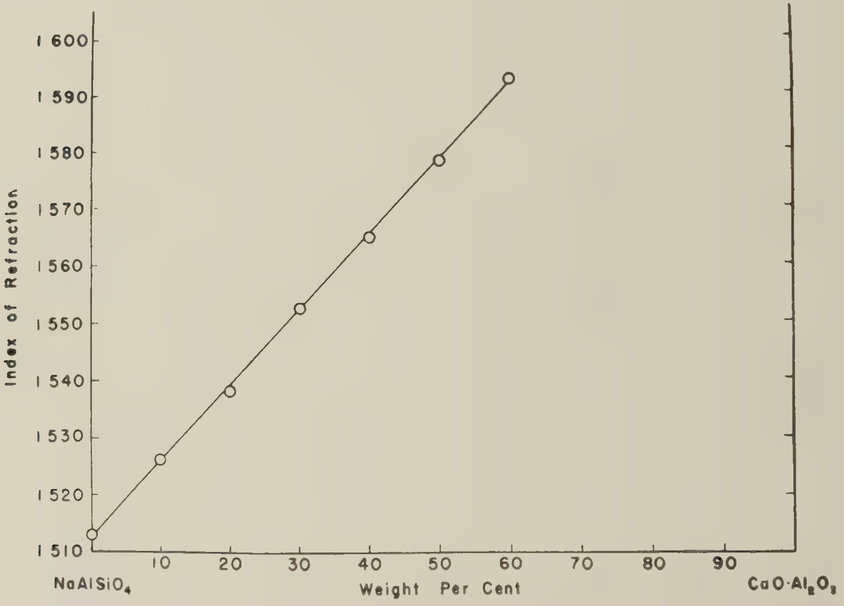

FIG. 3. Refractive indices of the glasses in the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$.

The indices of pure synthetic nepheline (Hexagonal $NaAlSiO_4$), determined by Bowen (1912, p. 566), are $\epsilon = 1.533$ and $\omega = 1.537$. He found that the indices of the limiting solid solution with anorthite are $\epsilon = 1.539$, $\omega = 1.537$. Solid solution of albite in nepheline lowers the indices (Foster, p. 157). Unusually high indices were noted by Smalley in nephelines crystallizing from the system $NaAlSiO_4$-$Ca_2Al_2SiO_7$, and by the writer (1947) in the system $CaAl_2Si_2O_8$-$Ca_2Al_2SiO_7$-$NaAlSiO_4$. Smalley found values as high as 1.552 in crystals from melts of 35 per cent gehlenite. The present study, which is primarily an outgrowth of these results, has produced nepheline solid solutions with indices above 1.590. The optic sign changes from negative to positive, passing through a range of optically isotropic crystals. It is very likely that the material in solid solution producing these extremely high values of refractive index is the same as that responsible for the high values observed in the two works last mentioned.

Nepheline crystallizes from melts in well formed prismatic crystals with basal pinacoid. In the present study, however, nepheline solid solutions do not occur at liquidus temperatures, but as the secondary or tertiary phase. When crystallized under these conditions, or below the solidus curve, euhedral crystals would not be expected to form. Thus the nepheline solid solutions here produced appear as xenomorphic crystals, often containing the other phases that may be present as inclusions.

$CaO \cdot 2Al_2O_3$

The 1:2 compound of lime and alumina has been for the most part improperly identified as $3CaO \cdot 5Al_2O_3$ in this country since its description in 1909 (Shepherd, Rankin, and Wright, 1909). A note by the present author (Goldsmith, 1948) discusses this improper formulation and summarizes the data on hand for $CaO \cdot 2Al_2O_3$. The 1:2 compound is monoclinic (Lagerqvist, Wallmark, and Westgren, 1937), although optically uniaxial or very nearly so. Wright noted the uniaxial character and determined the indices as $\epsilon = 1.651$ and $\omega = 1.617$ in the original (1909 description). $CaO \cdot 2Al_2O_3$ melts incongruently at a temperature of about 1765° C. (Tavasci, 1937).

In the present study $CaO \cdot 2Al_2O_3$ forms as well defined lath-shaped crystals, terminated with asymmetrical dome-like faces. Occasionally small crystals are blocky. The maximum extinction angle is highly inclined to the elongation, although the interference figures obtained are either uniaxial or biaxial with a very small value of 2V. The refractive indices appear to be the same as those described by Wright indicating little if any solid solution. The 1:2 compound was identified with certainty on the basis of its x-ray diffraction pattern as well as by optical means.

The end-member compound of the system $CaO \cdot Al_2O_3$, does not form in any of the mixtures studied, i.e., up to 80 per cent $CaO \cdot Al_2O_3$ by weight. It was, however, prepared in pure form by sintering of carefully mixed Al_2O_3 and $CaCO_3$, and the optical properties and x-ray pattern were checked against published data. Wright (1909) lists $\alpha = 1.641$, $\beta = 1.654$, and $\gamma = 1.661$ but could not determine whether the compound was monoclinic or triclinic. The melting point is given as $1600 \pm 5°$ C. by Brownmiller and Bogue (1932, p. 505).

β-Al_2O_3

β-Al_2O_3 is here encountered as both a primary and secondary phase, occurring as thin hexagonal plates exhibiting high birefringence and parallel extinction when viewed on edge. β-Al_2O_3 is optically negative, as indicated by the positive elongation of the platy crystals. The relation between β-Al_2O_3 and corundum and the effects of soda volatilization on the abundance of β-Al_2O_3 will be more fully discussed in a later section.

Corundum (Al_2O_3)

Synthetic corundum forms as rather small blocky crystals, for the most part somewhat elongated in the direction of the *c* axis. Some of the crystals, particularly when quite small, have rounded corners. The tendency toward elongation generally gives a negative sign of elongation, as corundum is optically negative. The refractive indices could not be determined on the crystals here encountered embedded in glass, but Wright (1909, p. 321) gives values of $\omega=1.768$ and $\epsilon=1.760$ on synthetic crystals. Corundum is most easily identified in this system by its low birefringence, parallel extinction, and sign of elongation, although when occurring along with large amounts of $CaO \cdot 2Al_2O_3$ its presence may be difficult to detect.

III. COMPLEXITY OF THE SYSTEM

If the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$ were binary, no more than three phases could coexist under equilibrium conditions, and as many as three phases only under invariant conditions at a point on the equilibrium diagram. The condensed phase rule, $P+F=C+1$, as applied to systems in which the vapor phase is negligible, expresses this relationship. Inspection of the equilibrium diagram, Fig. 2, shows that three phases coexist in several fields, and in two fields there are four phases present. At one point five phases coexist, the maximum number that can be present at an invariant point in a four component system. The composition of three of the crystalline phases, $CaO \cdot 2Al_2O_3$, β-Al_2O_3, and corundum cannot be expressed in terms of the end members; in a truly binary system all phases can be so expressed. The number of phases that coexist, as well as the fact that the composition of the phase assemblages can be expressed only in terms of the four constituent oxides, make it apparent that the system is quaternary.

Complexity may be introduced in a system by virtue of the formation of mix crystals whose composition cannot be expressed in terms of the composition of the end members of the system. Behavior of this sort has been previously discussed by the author (1947). In the system under consideration, however, complex solid solutions are not primarily responsible for its non-binary nature, rather the intrusion of the phases $CaO \cdot 2Al_2O_3$, β-Al_2O_3 and corundum introduce the complexity. This is a consequence of the stability fields of these substances, within the quaternary tetrahedron, intersecting the join $NaAlSiO_4$-$CaO \cdot Al_2O_3$. A four component system must be represented by a three dimensional figure; it should be emphasized that the equilibrium diagram (Fig. 2) cannot be interpreted as a binary diagram would be. Particularly above solidus temperatures, the compositions and the proportions of phases cannot be precisely determined from the diagram, and the curves do not represent lines of univariant equilibrium.

Relations in the system become less complex as a result of the inversion of carnegieite to nepheline, and will shortly be considered in more detail. Indeed, binary relations are developed at lower temperatures (below the carnegieite to nepheline inversion range) over a considerable portion of the system as a result of the rather large amounts of calcium aluminate taken in solid solution by nepheline.

IV. RELATIONS ABOVE THE SOLIDUS, AND THE EFFECT OF SODA VOLATILIZATION

The carnegieite liquidus curve falls as a straight line from the melting temperature of pure carnegieite (1526° C.) to a point at approximately 32 per cent $CaO \cdot Al_2O_3$ where it is intercepted by the intruded field of β-Al_2O_3. From approximately 32 per cent to 46 per cent $CaO \cdot Al_2O_3$, β-Al_2O_3 becomes the primary phase, the liquidus curve showing a general convex upward configuration. The β-Al_2O_3 curve is in turn intercepted by that of $CaO \cdot 2Al_2O_3$, which becomes the primary phase from 46 per cent to at least 80 per cent $CaO \cdot Al_2O_3$, beyond which composition no preparations were made. The liquidus temperature of the mixture of 80 per cent $CaO \cdot Al_2O_3$, 20 per cent $NaAlSiO_4$ was not determined, because of the refractory nature of this mixture. The primary phase, however, was the 1:2 compound. Although the compound $CaO \cdot Al_2O_3$ was not encountered, a stability field at liquidus temperatures exists, but is not shown on Fig. 2. Examination of the phase diagram for the system CaO-Al_2O_3-SiO_2 (Sosman and Anderson, 1942) gives an indication of the approximate location of this boundary. The compound $CaO \cdot Al_2O_3$ is quite near the boundary curve between the fields of $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$, improperly identified as $3CaO \cdot 5Al_2O_3$ on the above diagram, and the supposition that the field of the 1:1 compound is cut off by the field of the 1:2 compound a very short distance within the quaternary system is very likely. Thus the field of $CaO \cdot Al_2O_3$ would extend on Fig. 2 but a few per cent into the diagram.

β-Al_2O_3 exists as the secondary phase except over the short range where it becomes the primary phase. At approximately 50 per cent $CaO \cdot Al_2O_3$, or where the 1:2 compound becomes the primary phase, β-Al_2O_3 disappears however, and corundum takes its place, continuing as the secondary phase to the limit of composition studied. β-Al_2O_3, never really quantitatively abundant, also appears to fade out between 5 and 10 per cent $CaO \cdot Al_2O_3$. A maximum and minimum limit to its field can be detected in the mixture of 10 per cent $CaO \cdot Al_2O_3$, but no β-Al_2O_3 was found in the mixture of 5 per cent $CaO \cdot Al_2O_3$. The lower limit of the field of β-Al_2O_3 falls below the solidus, and is rather well defined between 10 and 40 per cent $CaO \cdot Al_2O_3$, but cannot be traced beyond the 40 per cent mixture. In the 50 per cent and greater mixtures, below solidus temperatures, very rare β-Al_2O_3 or corundum may occur, but no definite lower limit to the field can be fixed.

The upper limit of the stability field of carnegieite continues on under the primary phase field of β-Al_2O_3, where carnegieite becomes the secondary phase. Beyond 40 per cent $CaO \cdot Al_2O_3$, carnegieite becomes the tertiary phase; the upper temperature limit of the field of carnegieite slowly rises, and carnegieite is still evident in the mixture of 80 per cent $CaO \cdot Al_2O_3$—20 per cent $NaAlSiO_4$.

The upper boundary of the carnegieite-nepheline inversion range shows a rather small temperature variation throughout the greater portion of the system. From the inversion point of pure nepheline and carnegieite at 1254° C., the boundary rises sharply to 1342° C. at the composition 95 per cent $NaAlSiO_4$—5 per cent $CaO \cdot Al_2O_3$. The upper limit of inversion then decreases slightly to a value of approximately 1332° C. between 10 and 20 per cent $CaO \cdot Al_2O_3$, beyond which it rises slowly, attaining a value of 1350° C. at 60 per cent $CaO \cdot Al_2O_3$. Nepheline does not occur as a primary phase; it is formed at or near solidus temperatures. The lower boundary of the inversion range was not determined, because of the metastable persistence of carnegieite at low temperatures. There is some evidence however, that the carnegieite that forms in the mixture of 60 per cent $CaO \cdot Al_2O_3$ is practically all transformed to nepheline at a temperature in the neighborhood of 1300° C. A sub-solidus curve delimiting the lower portion of this field has thus been indicated with dashed lines on Fig. 2.

The temperature of complete crystallization, represented by the solidus curve, drops sharply from the melting point of pure carnegieite at 1526° C., to 1342° C. at 5 per cent $CaO \cdot Al_2O_3$. It then continues, coincidentally with the nepheline carnegieite inversion curve, to 30 per cent $CaO \cdot Al_2O_3$ at which point the inversion curve rises above it. The solidus curve was not followed beyond 60 per cent $CaO \cdot Al_2O_3$, where the temperature of complete solidification is 1332° C. It is to be noted that over most of the range studied the temperature of complete crystallization varies but a few degrees. Indications are, however, that beyond the 60 per cent value the curve rises fairly rapidly.

Soda Volatilization

The loss of soda by volatilization in preparations here considered merits some discussion. In melting the glass batches used for the equilibrium studies an appreciable weight loss was observed. This loss did not diminish with decreasing Na_2O content, i.e., as $CaO \cdot Al_2O_3$ was increased in the system, as might be expected if the loss were due solely to straightforward vaporization of soda. No attempt was made to evaluate quantitatively soda loss as a function of composition, but it appears that addition of the $CaO \cdot Al_2O_3$ tends to drive Na_2O from the batch. This effect is worthy of separate study; it is apparent that either alumina or lime tends to increase the rate of soda loss. The fact that the silica content of the mixtures is diminished concurrently with these additions may be important. The tendency for alumina to drive off soda has not been noted in the many studies dealing with these oxides, but there is evidence that lime may act in this manner. Madorsky (1931), in studying the possibility of obtaining potash from leucite-bearing rocks, shows that additions of $CaCO_3$ to wyomingite with subsequent heating above 1100° C. increases the loss of potash by vaporization. The same effect, involving large losses of K_2O from wyomingite, is reported by Hignett and Royster (1931), who used both $CaCO_3$ and CaO in a small blast furnace. This effect was greatly amplified if in addition to the lime a halogen salt such as $CaCl_2$ were added so that the more volatile KCl was driven off; the chloride volatilization, however, is not to be considered here. Although potash is more volatile than soda there is little doubt that the two alkalis would behave qualitatively in similar fashion. The present investigation also seems to indicate that CaO tends to drive alkalis from alkali-silicate mixtures. In a discussion of this question, N. L. Bowen* has stated that some of his investigations, particularly involving mixtures of a sodium aluminate and a calcium silicate, have led him to suspect that this phenomenon takes place.

This action is observed to take place in the fused mass (liquid state) as well as during reaction of the original batch before melting is complete, and may be the result of bond weakening in the glass with increased basicity. Loss of soda can be corrected for in preparing the original batches, but no corrections can be made during the equilibrium run itself. Runs of as short a time as possible that would insure equilibrium were made, although this precaution was not found necessary at temperatures somewhat below the solidus.

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* Personal communication.

The effect of soda loss during an equilibrium run is rather marked in certain parts of the system. In the region 30–40 per cent $CaO \cdot Al_2O_3$, where β-Al_2O_3 and carnegieite are the primary and secondary phases, relations are strongly affected by the length of time the charge is held at near-liquidus temperatures. At the composition 70 per cent $NaAlSiO_4$—30 per cent $CaO \cdot Al_2O_3$, carnegieite is the primary phase, appearing at 1396° C. in runs of 30 minutes' duration. Under these conditions, β-Al_2O_3 appears as the secondary phase, at 1382° C. If, however, the charge is held for three hours, β-Al_2O_3 crystals, and *no* carnegieite, are found, even though the temperature be dropped 10° C., to 1386° C. A run made at 1420° C. for $3\frac{1}{2}$ hours showed only liquid to be present in the envelope containing the charge, except where present as thin films (in the edges of the platinum containing envelope); the thin portions of the quenched glass contained abundant β-Al_2O_3. Thus β-Al_2O_3 persists even at temperatures considerably above the liquidus, if a rather large surface is present as in the films of glass, to make soda volatilization more effective. In the mixture of 35 per cent $CaO \cdot Al_2O_3$, abundant β-Al_2O_3 is present in runs over three hours at 1425° C.; the β-Al_2O_3 liquidus on a 30 minute basis is 1408° C. at this point. In the 40 per cent $CaO \cdot Al_2O_3$ mixture, the 30 minute phase assemblage at 1348° C. is glass, β-Al_2O_3, very sparse carnegieite, and very rare $CaO \cdot 2Al_2O_3$. This same charge, when held three hours, is found to have crystallized rather large amounts of $CaO \cdot 2Al_2O_3$ and in addition is rather frothy, indicating loss of a volatile ingredient. $CaO \cdot 2Al_2O_3$ appears at a temperature of 1350° C. in 30 minute runs at this composition, but if the temperature is raised to 1360° and held for two hours, $CaO \cdot 2Al_2O_3$ is present along with β-Al_2O_3.

These data make it evident that the quantity and even the presence of the non-sodic or soda-poor phases such as the 1:2 compound and β-Al_2O_3 are influenced by volatization of soda; loss of soda induces the crystallization of these phases. Conversely, replacement of carnegieite by β-Al_2O_3 at temperatures below the carnegieite liquidus, as seen in the 30 per cent $CaO \cdot Al_2O_3$ mixture, indicates suppression of the sodic phase by volatilization. The liquidus curve for β-Al_2O_3 as drawn on Fig. 2 is an arbitrary curve based on mixtures run for 30 minutes. Longer runs would fix the liquidus at a considerably higher level, and indeed, it is likely that as now located it is somewhat above what it would be if determinations were made in a closed system.

The problem of attaining equilibrium and maintaining composition is a difficult one when volatilization losses become significant. Removal of soda makes the already existing non-binary system even more complex.

In a quaternary (condensed) system five phases can coexist at equilibrium only at a point of fixed composition and temperature. In the narrow four-phase field of $CaO\cdot 2Al_2O_3$, carnegieite, nepheline, and glass (the wedge-shaped field just above the solidus beyond 40 per cent $CaO\cdot Al_2O_3$), several runs of approximately three hours show five phases —the above four plus very rare β-Al_2O_3. In the other small four-phase field of nepheline, carnegieite, β-Al_2O_3, and glass (adjacent and to the left of the above field on Fig. 2), a similar effect is noted. At the composition 50 per cent $CaO\cdot Al_2O_3$ and a temperature of 1340° C., the four-phase assemblage is found in runs of 30 minutes. Runs of three hours or more show crystals of $CaO\cdot 2Al_2O_3$ as well—a fifth phase. The coexistence of five phases over a range of temperature is indicative of failure of equilibrium. Continuous loss of soda and the resulting continuous composition change with time makes impossible the establishment of equilibrium, and volatilization is undoubtedly the explanation for this effect. A true five-phase point does exist, at 1344° C. and at a composition of approximately $39\frac{1}{2}$ per cent $CaO\cdot Al_2O_3$. A second five phase point is inferred at approximately 50–52 per cent $CaO\cdot Al_2O_3$, and at a temperature of approximately 1334° C. It should be stated, however, that the true relations in this portion of the diagram are made somewhat uncertain by reason of the above discussed complications due to loss of soda.

The presence or absence of β-Al_2O_3 as a function of soda volatilization is important in the above considerations. One cannot always decide whether its absence may not be due to insufficient time to establish equilibrium, or its presence due to an excessively long run resulting in significant soda loss. The earlier mentioned uncertainty as to the lower limits of the field of β-Al_2O_3 may possibly be explained on this basis.

V. Sub-Solidus Relations

In the runs made at temperatures below the carnegieite-nepheline inversion, carnegieite was always found, in all of the compositions studied. The scarcity of carnegieite in certain runs was the basis for the roughly sketched curve on Fig. 2 delimiting its lower limit of existence, but accurate determinations were not made as the inversion to nepheline was never observed to be complete. As the temperature of devitrification of the glasses was lowered, more carnegieite was obvious, it being apparent that carnegieite was forming at temperatures well below its field of stability.

Extended runs at relatively low temperatures showed rather conclusively that even in the stability field of nepheline, carnegieite is the *first* phase to crystallize from the glass. For example, crushed glass of the composition 40 per cent $NaAlSiO_4$—60 per cent $CaO\cdot Al_2O_3$ held five days at 795° C. showed small amounts of carnegieite "eating" into the glass. Re-examination after an additional 10 days showed some glass with carnegieite "replacing" it, but the bulk of the product was now nepheline solid solution. In the mixture of 50 per cent $NaAlSiO_4$—50 per cent $CaO \cdot Al_2O_3$, the crushed glass when held five days at 795° C. appeared under the microscope as illustrated in Fig. 4.

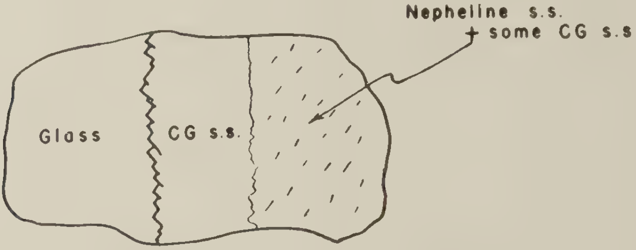

FIG. 4. Fragment, initially all glass. Note "shark-teeth" like aspect of carnegieite (crystal faces) at the glass-carnegieite contact.

Re-examination after an additional 10 days shows that the entire fragment has been devitrified, consisting of nepheline and a small amount (perhaps 10 per cent) of carnegieite. To determine the possible effect of lime and alumina on this metastable crystallization, glass of the composition of the pure end-member ($NaAlSiO_4$) was devitrified. Holding pure $NaAlSiO_4$ glass at 795° C. for five days produced virtually pure carnegieite; after 15 days no more than a trace of nepheline could be detected. The inversion temperature of the pure compound is 1254° C., yet it is here obvious that carnegieite forms initially far below its stable inversion point. The additions of $CaO \cdot Al_2O_3$ in the system are not responsible for this effect, but rather tend to accelerate the inversion once the carnegieite has crystallized.

Bowen (1912, p. 560) noted that at a few degrees below the stable inversion glass crystallizes as both nepheline and carnegieite. He stated that "It seems possible that the unstable glass in assuming the stable form nephelite passes through the 'less unstable' form carnegieite which may persist for a considerable time and is therefore found in the quenched products." Bowen, however, did not observe the formation of carnegieite at temperatures well below the inversion point. An analogous behavior is well known in the case of SiO_2 where it is found that cristobalite, the high temperature form of silica (stable only above 1470° C.), is the first phase to crystallize from silica glass throughout the whole devitrification range and tends to persist metastably for long periods of time.

Bowen's explanation for the carnegieite formed below its inversion point is quite reasonable, particularly in view of the lack of knowledge in 1912 on the structure of glasses and crystals. A plausible explanation of this phenomenon from another point of view exists when one considers that the glass represents the most disordered state of the silicate material. The high temperature crystalline phase is most closely akin to the glassy state; in silica glass the random SiO_4 network requires but slight re-arrangement or ordering to form cristobalite. The high temperature form might thus be expected to be the one most readily crystallized, even well below its stability range, especially in materials in which ionic movement and re-arrangement is inhibited because of high viscosity. Carnegieite has the same atomic arrangement as critobalite; glasses from which carnegieite form as the primary phase, therefore, very likely have a random structure very similar to that of carnegieite. At higher temperatures, just below the carnegieite-nepheline inversion temperature, the decreased viscosity of the glass and resulting ease of ionic movement allows nepheline to form directly, but it is not improbable that the high temperature form crystallizes first and then rapidly inverts to the low temperature modification.

The fact that carnegieite tends to persist as well as to form metastably has already been noted. Carnegieite formed in mixes containing appreciable amounts of $CaO \cdot Al_2O_3$ inverts to nepheline more rapidly than does pure $NaAlSiO_4$, but even in the mixture of 50 per cent $CaO \cdot Al_2O_3$ carnegieite is intermixed with the nepheline solid solution after 25 days at 795° C. Beyond 50 per cent $CaO \cdot Al_2O_3$ the inversion is again slowed, as in the 60 per cent $CaO \cdot Al_2O_3$ mix a very significant amount of carnegieite was found in runs of 35 days at 795°–900° C. Equilibrium is of course not established in these runs—to do so would require an unduly long period of time. The reconstructive transformation is very slow, especially at low temperatures and in the absence of a liquid phase.

The Carnegieite and Nepheline Solid Solutions

CARNEGIEITE.—$CaO \cdot Al_2O_3$ enters the structure of carnegieite to the extent of 5 per cent by weight. The carnegieite of this composition has a maximum refractive index of 1.521, and a birefringence somewhat less than that of the pure $NaAlSiO_4$. The inversion to a triclinic form takes place in carnegieite of this composition, and the resulting polysynthetic twinning is present. As the $CaO \cdot Al_2O_3$ content of the system is increased, however, a continued, although rather small, increase in refractive index is observable, and inversion to the triclinic form does not take place in the carnegieite that crystallizes from mixes with more than approximately 20 per cent $CaO \cdot Al_2O_3$. The continued rise in index and the stabilization of the isometric lattice indicate that more solid solution in carnegieite takes place than the 5 per cent $CaO \cdot Al_2O_3$ indicated by the thermal evidence. This additional solid solution cannot, however, be binary in nature. Either lime, alumina, or some combination of the two in proportions other than the 1:1 ratio enter the carnegieite structure. The exact nature of the non-binary solid solution cannot be determined from the data of the present system.

Stabilized isometric carnegieite has also been observed to form in portions of the system Na_2O-Al_2O_3-SiO_2, by J. F. Schairer.* Schairer and Bowen (1947, p. 197) have described solid solutions of carnegieite with $Na_2O \cdot Al_2O_3$; it is possible that this solid solution might also be forming in the present system.

The *x*-ray powder pictures of the carnegieite solid solutions are sufficiently different from the pattern of pure carnegieite ($NaAlSiO_4$) that even the 5 per cent solid solution with $CaO \cdot Al_2O_3$ shows up markedly. The most obvious difference in the two patterns is the development of four lines of rather high *d* value in the solid solution. No attempt will be made here to present or interpret *x*-ray data—this will be done in a future note on carnegieite and nepheline.

NEPHELINE.—The exact limit of $CaO \cdot Al_2O_3$ solid solution in nepheline was not determined, because of the previously mentioned difficulty of obtaining crystals free of carnegieite. Mixtures up to and including 60 per cent $CaO \cdot Al_2O_3$ were crystallized with but two phases, however, nepheline and carnegieite. It can thus be concluded that nepheline takes at least 60 per cent $CaO \cdot Al_2O_3$ in solid solution. It is probable that considerably less than 80 per cent $CaO \cdot Al_2O_3$ enters the nepheline structure, as evidenced from runs on the mixture of this composition. No definite statement can be made on this point, however, as the original preparation of 80 per cent $CaO \cdot Al_2O_3$ contained crystals of the 1:2 compound; a homogeneous glass could not be obtained with which to carry out crystallizations at the temperatures of the nepheline field.

The mixture of 60 per cent $CaO \cdot Al_2O_3$ when crystallized at 800° C. shows no trace of any calcium-aluminate phase, only nepheline solid solution and carnegieite being evident. *X*-ray as well as optical determinations were made. If, however, some calcium aluminate were present, it would not necessarily mean that the solid solution limit had been passed, as long as some carnegieite was intermixed. The reason for this is that the carnegieite takes but a small amount of $CaO \cdot Al_2O_3$ in solid solution, whereas nepheline takes very much more. The carnegieite, which under equilibrium conditions would exist as nepheline, thus represents "potential" nepheline, capable of taking up additional $CaO \cdot Al_2O_3$.

Solid solution of $CaO \cdot Al_2O_3$ in nepheline produces a steady rise in index of refraction. Values of as high as $\epsilon = 1.600$ and $\omega = 1.593$ are reached in the nepheline crystals from the 60 per cent $CaO \cdot Al_2O_3$ mix. The optic sign changes from negative in pure nepheline, to positive, passing through a zone of optically isotropic crystals at approximately 20 per cent $CaO \cdot Al_2O_3$. Beyond this isotropic composition, the birefringence slowly increases up to the limiting composition studied. Figure 5 is a refractive index-composition diagram for the nepheline solid solution. As in the carnegieite, the solid solution can be readily detected by x-ray diffraction. The most obvious changes with solid solution observed in the powder pattern are the development of a 100 line not present in pure $NaAlSiO_4$, a great intensity increase in the 110 line, and the disappearance in the solid solution of the 200 reflection.

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* Unpublished data by J. F. Schairer and N. L. Bowen.

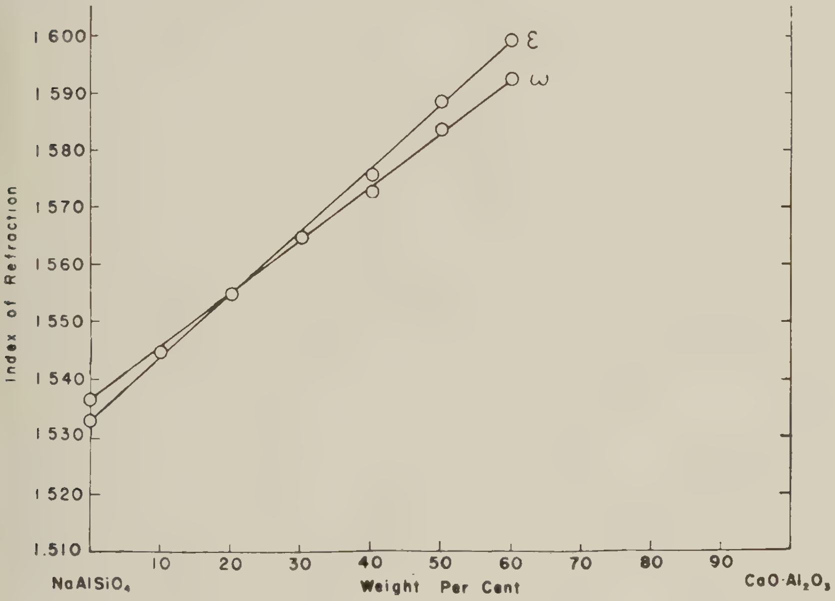

FIG. 5. Refractive indices of the nepheline solid solutions in the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$.

As earlier mentioned, the system becomes simplified below the carnegieite-nepheline inversion range because of the $CaO \cdot Al_2O_3$ taken up by the nepheline: binary relations exist at least up to the limit of solid solution. Thus although the general $NaAlSiO_4$-$CaO \cdot Al_2O_3$ relations are quite complex, the *nepheline*-$CaO \cdot Al_2O_3$ relations are comparatively uncomplicated. The higher temperature complexities begin to simplify as soon as nepheline begins to form in the system; as it crystallizes it takes up lime and alumina that in the presence of carnegieite would form independent phases. The binary solid solution of nepheline and $CaO \cdot Al_2O_3$ produces a single-phase field of nepheline solid solutions up to at least 60 per cent $CaO \cdot Al_2O_3$.

In mixtures of 50–60 per cent $CaO \cdot Al_2O_3$, and at temperatures below the solidus and above the field of nepheline solid solutions, the phases nepheline, carnegieite, and $CaO \cdot 2Al_2O_3$ are found to coexist. If lime and alumina were taken in both carnegieite and nepheline in the 1:1 ratio, the 1:2 compound could not form; the calcium aluminate phase would of necessity be the 1:1 compound. The fact that the 1:2 compound is formed indicates that in this field either the carnegieite, the nepheline, or both form non-binary solid solutions. The tendency is seen throughout the system for alumina-rich phases to precipitate (corundum, β-Al_2O_3, and $CaO \cdot 2Al_2O_3$ rather than $CaO \cdot Al_2O_3$), and if any of these phases persist, in the absence of liquid, with nepheline and carnegieite, it is obvious that lime in excess of the 1:1 lime-alumina ratio is in the structure of the nepheline and/or the carnegieite. It has been seen that the carnegieite solid solution is non-binary, so that it is probable that the tendency to form $CaO \cdot 2Al_2O_3$ is an indication that excess CaO is present in the carnegieite of this portion of the system. The possibility that the nepheline in this field also contains excess CaO cannot be precluded, however.

VI. THE β-Al_2O_3-CORUNDUM RELATIONS

The field of β-Al_2O_3 is known to extend well toward the silica rich corner of the Na_2O-CaO-Al_2O_3-SiO_2 tetrahedron. The work of Gummer (1943, p. 506) has shown that a portion of the anorthite-wollastonite-nepheline plane is penetrated by the field of β-Al_2O_3; the position of this plane can be seen in Fig. 1. The problem of the composition of β-Al_2O_3 has been earlier discussed by the present writer (Goldsmith, 1947, p. 384), it being suggested that β-Al_2O_3 might be a "stuffed lattice," in which Na atoms assume random interstitial positions in an Al_2O_3 network. This explanation was used to account for the disagreements of different investigations on the soda content, as no fixed soda-alumina ratio is required in a structure of the proposed type. Schairer and Bowen (1947, p. 198) have indicated that β-Al_2O_3 is metastable with respect to corundum; it is converted to corundum on long heating. The above view of the β-Al_2O_3 structure was also considered consistent with this conversion to corundum, as the interstitial Na atoms, given sufficient time, might be squeezed out of the structure.

The present investigation tends to strengthen this picture of β-Al_2O_3. Between 40 and 50 per cent $CaO \cdot Al_2O_3$ the field of β-Al_2O_3 changes over to a field of corundum. It is thus likely that the change from a field of β-Al_2O_3 to one of corundum takes place throughout the Al_2O_3 rich corner of the tetrahedron, i.e., that the three dimensional corundum field is continuous with that of β-Al_2O_3. This is equivalent to saying that when sufficient soda (or in the general case, sufficient alkali) is present in the melt β-Al_2O_3 crystallizes, and when less than the limiting value of alkali is present, corundum is formed. Inasmuch as some compositional change is involved, the β-Al_2O_3-corundum relation can hardly be called an inversion in the sense that temperature or pressure dependent inversions are defined. Although the results of Schairer and Bowen indicate that β-Al_2O_3 is metastable, it might be a stable form under certain conditions, for example, where high alkali ion activity exists in the melt in equilibrium with the crystals.

VII. Petrologic Considerations

Several points of possible interest to the igneous petrologist are suggested by the present investigation, although it should be emphasized that the melts of the system here studied do not correspond in composition to any natural magmas.

Alkaline rocks of the phonolite-nepheline syenite type are frequently associated with limestone. If molten or magmatic material were injected into the limestone it might be expected that some contamination or reaction with the CaO of the limestone would result. Corundum is found in and associated with certain of the nepheline syenites. The tendency for formation of β-Al_2O_3 (or corundum) as a result of soda volatilization when CaO is added to the system here studied, and the presence of corundum and associated lime rocks in nepheline syenite areas is suggestive of a related effect. The tendency of β-Al_2O_3 to go over to corundum has already been mentioned—even though β-Al_2O_3 may be first precipitated, corundum might be the end result. Soda "metasomatism" or enrichment of associated rocks in sodic minerals could also be a consequence of the freeing of soda by the above process. S. J. Shand has stated that he has often had reason to suspect that soda has been expelled at limestone contacts,* and made this assumption in a paper dealing with the granite-syenite-limestone complex of Palabora. (Shand, 1931, pp. 99–101.) The phenomena above discussed, if operative, would be influenced by a "closed" vs. an "open" system, and the depth at which intrusion took place might be here important. In a fully closed system from which volatiles could not escape alumina formation would at least be inhibited, and no soda loss to the surroundings would take place. The usefulness of these observations as possible criteria for the determination of magmatic vs. replacement origin of these rocks cannot, however, be evaluated on the basis of the experimental system.

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* Personal communication from S. J. Shand.

The large amounts of lime taken up by the nephelines that crystallize in the system $NaAlSiO_4$-$CaO \cdot Al_2O_3$ might lead one to expect that such lime and alumina-rich nepheline might be found in rocks, especially those that crystallized from a magma that was associated with lime rich material. Most analyses of natural nephelines show an excess of SiO_2, whereas the nephelines of the present system are undersilicated. It must be remembered, however, that the present system is deficient in silica as compared to natural systems, and it is likely that in nature the silica content is always sufficient so that feldspar, rather than an aluminate, forms solid solutions with nepheline. Enrichment of a natural system in CaO by such a process as limestone contamination need not result in lime-enriched nepheline at any rate; feldspar or other lime containing minerals could well have a "buffer" effect, and take up considerable amounts of CaO before nepheline would do so. It should also be considered that the lowest temperature of the present investigation was approximately 800° C.; the stability of the nepheline-calcium aluminate solid solution at lower temperatures is not known. Nepheline bearing rocks for the most part have probably formed at temperatures below 800° C., where the solid solution relations might be significantly different.

Acknowledgment

This work was done in conjunction with a research program made possible by financial assistance from the Office of Naval Research. The writer is also indebted to Dr. Tom. F. W. Barth for his discussions and criticisms, and to Mrs. Ursula Chaisson, who took all of the x-ray pictures used in the investigations.

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THE MOORE COUNTY METEORITE: A FURTHER STUDY WITH COMMENT ON ITS PRIMORDIAL ENVIRONMENT

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Abstract

The Moore County meteorite in bulk composition resembles a Sudbury norite. The pyroxenes present were initially probably a single phase, pigeonite. This has undergone a complicated series of changes from which it is deduced that the temperature of the original environment was approximately 1135° C. and that the meteorite left this environment with catastrophic suddenness. Investigation of the fabric of the meteorite indicates a dimensional orientation of the plagioclase and pyroxene. The plagioclase *b* and *c* crystallographic axes and the pyroxene *c* axis tend to lie in one plane. The fabric is considered to represent primary layering developed by crystal accumulation on the floor of a magma chamber. Thus crystallization differentiation must have occurred in the original environment.

Introduction

The Moore County, North Carolina, meteorite, a eucrite, was described in considerable detail by Henderson and Davis (1936). The comment was made that "there is very little bond between the component minerals. In fact the minerals can be easily separated by lightly rubbing the fingers over the surface . . . ." "It was found to be almost impossible to make thin sections of this meteorite without causing the mineral grains to completely separate one from another." The present paper is occasioned by the fact that an excellent thin section has now been obtained as a result of which additional significant relations can be recorded and certain modifications of the original paper are in order. G. S. Rev made the thin section after impregnating the material with bakelite.

Description

The meteorite is unique in that it has very little native metal and in that it closely resembles in chemical composition, mineralogy, and texture a terrestrial plutonic igneous rock. The chemical analysis is given in Tables 1 and 2 along with a norite of similar composition from Sudbury, Ontario, for comparison.

The meteorite consists almost entirely of pyroxene and calcic plagioclase. A small amount of tridymite is present interstitial to the above minerals, and small grains of black opaque minerals may be seen in the section. The tridymite contains exceedingly minute colorless needles which appear to be apatite. Sporadic aggregations of equally minute opaque rounded blebs and specks are present in the plagioclase and pyroxene along fracture planes.

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TABLE 1

	Moore City* Eucrite	Sudbury† Norite
SiO_2	48.16	46.69
Al_2O_3	15.57	14.23
Fe_2O_3	1.90	2.00
FeO	13.98	12.86
MgO	8.41	8.15
CaO	11.08	13.32
Na_2O	.45	.98
K_2O	.09	.00
H_2O+	—	.08
H_2O-	—	—
TiO_2	.32	1.28
Cr_2O_3	.44	—
P_2O_5	—	.19
MnO	.31	.11
S	.30	.12
	101.01	100.01
−O for S	.15	
	100.86‡	

* Analyst E. P. Henderson.

† Washington's Tables p. 666.

‡ Fe_2O_3 was reported as determined, but a considerable part of this is metallic Fe. If all of it is calculated as Fe the summation becomes 100.28.

THE PYROXENE

The bulk of the pyroxene present is pigeonite. It has beautifully developed augite lamellae parallel to {001}. These can readily be seen in the photomicrograph Fig. 1. The augite lamellae are interpreted as having developed in an original homogeneous pigeonite by exsolution during cooling as elaborated further below. Thus the bulk chemical composition of the pyroxene given in Table 3 is believed to represent the composition of the original homogeneous pyroxene crystals which crystallized from a magma in the primordial environment of the meteorite. A further alteration of the pyroxene has taken place, namely the inversion of a small amount of the pigeonite to hypersthene. Small roughly quadrilateral areas bounded by cleavages and augite lamellae have inverted to hypersthene in a few of the pigeonite crystals. This hypersthene is identical to the orthopyroxenes of the Bushveld type described by Phillips and Hess (1938, 1940) and has within it the very fine exsolution lamellae of clinopyroxene parallel to the {100} plane of the orthopyroxene which is characteristic of this mineral. Although the relationships between the pyroxene phases of the Moore County meteorite may seem to be complex from the above description, each step in the relations is clearly evident in the thin section and each is well known from terrestrial, igneous rock pyroxene relationships. Figure 2 portrays diagrammatically the sequence of changes which are assumed to have taken place in the pyroxene phases, Table 3 gives the bulk composition of the pyroxene as indicated by

TAPLE 2. NORMS

		Moore County, Eucrite			Sudbury, Norite		
Q		1.68			—		
*Pc	Or	.56	44.54		.00	42.57	
	Ab	3.67			8.38		
	An	40.31			34.19		
Di	Wo	6.03	11.97	50.13	12.99	25.69	51.39
	En	2.90			6.50		
	Fs	3.04			6.20		
Hy	En	18.10	38.16		10.40	20.70	
	Fs	20.06			10.30		
Ol	Fo	—			2.45	5.00	
	Fa	—			2.55		
†Mt		2.78	4.52		3.02	6.11	
Il		.61			2.43		
Cm		.67			—		
Ap		—			.34		
Py		.46			.24		
H_2O		—			.08		
		100.87	CIPW: 3,5,5,—,		100.07		

Mode‡

Tridymite	1.5
Plagioclase	40.0 ($Or_{.5}Ab_{10.7}An_{88.8}$)
Pyroxene	56.0 ($Ca_{10}Mg_{46}Fe_{44}$)
Opaque	2.5
Apatite	trace
	100.0

* $Or_1Ab_9An_{90}$

* $Or_0Ab_{20}An_{80}$

† Part of this is metallic iron.

‡ Only 3.5 sq. cm. available for traverse.

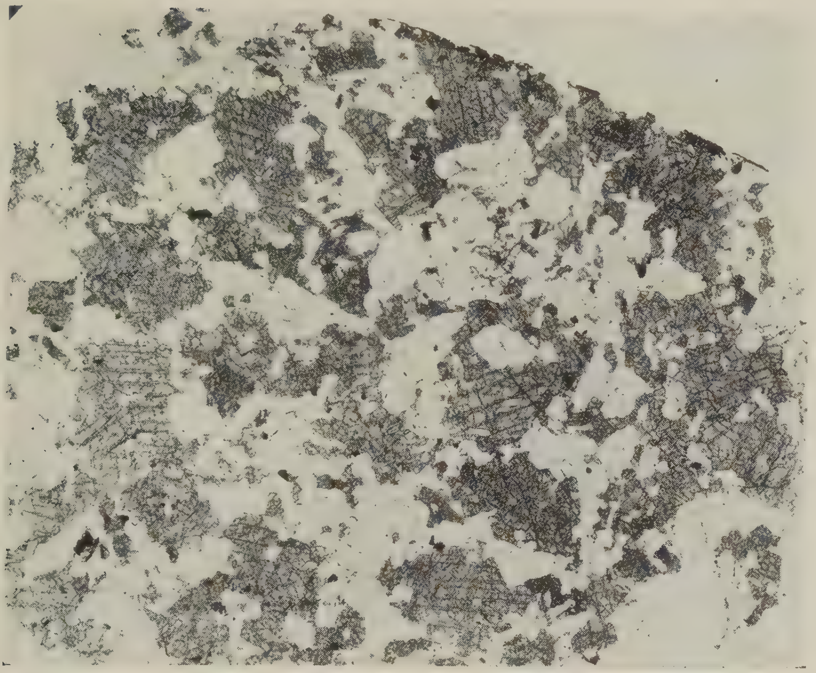

FIG. 1. Photomicrograph of thin section of Moore County, N. C. meteorite. Note augite lamellae in pigeonite are parallel to {100} plane. Dark glass of the crust on meteorite is shown on upper right hand edge. This fused crust is about 0.2 mm. thick. It is crowded with small bubbles and passes abruptly into fresh silicates.

chemical analysis and Table 4 gives the optical properties and estimated compositions of the four pyroxene phases now observable.

Pigeonite in terrestrial rocks is only known from rapidly cooled lavas or small hypabyssal intrusives. It has commonly been suggested, because of its association with lavas, that pigeonite may be a metastable phase brought about by rapid chilling. This view however is not substantiated by the petrographic evidence (Hess, 1941, Edwards, 1942). Pigeonite occurs in some volcanic rocks as phenocrysts (Mull, Hallimond 1914 and Hakone, Kuno 1936) evidently of intratelluric crystallization. It has also been a common constituent of plutonic igneous rocks but has in these cases inverted upon slow cooling to the orthorhombic form, hypersthene. Such hypersthenes contain exsolved plates of augite in a plane parallel to {001} of the original pigeonite and are easily recognized thereby as inverted pigeonites (Hess, 1941, Edwards, 1942). In the case of the Moore County meteorite the crystallization of the original pigeonite was followed, upon cooling, by the exsolution of augite plates parallel to {001}

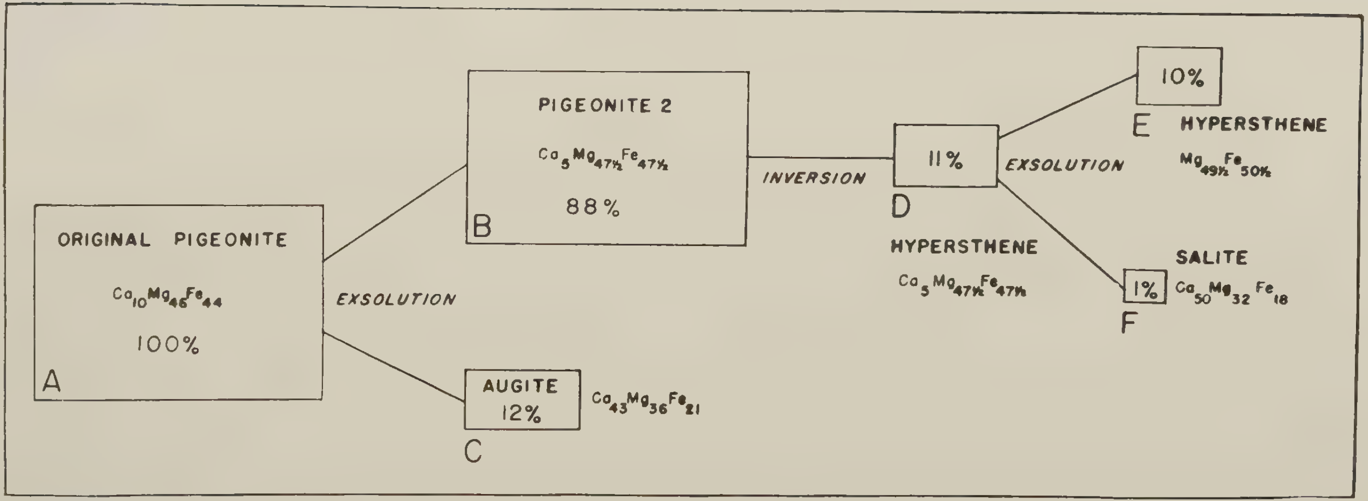

FIG. 2. Diagram to show relationships between the various pyroxene phases.
Solid Phase A Lacking; split into B and C by exsolution. (=chemical analysis)
Solid Phase B Present; approx. 77% of pyroxenic material remaining in the sample.
Solid Phase C Present; 12% of the pyroxenic material remaining.
Solid Phase D Lacking; split into E and F by exsolution.
Solid Phase E Present; approx. 10% of pyroxenic material remaining.
Solid Phase F Present; approx. 1% of pyroxenic material remaining.

TABLE 3. CHEMICAL COMPOSITION OF ORIGINAL PIGEONITE A

		Molecular Ratios	Ilmenite Magnetite	Remainder	Atomic Ratios				Cations to 6 O
SiO_2	49.37	8220		8220					
Al_2O_3	1.55	152		152	Si^{+4}	822		Z 843	
Fe_2O_3	1.83	115	− 70	45					
FeO	26.44	3680	−130	3550	Al^{+3}	30	21*		1.996
MgO	15.54	3854		3854			9		
CaO	4.60	820		820	Fe^{+3}	9			
TiO_2	.62	77	− 60	17	Fe^{+2}	355			
MnO	.37	52		52	Mg^{+2}	385		$X+Y$ 847	2.005
					Ca^{+2}	82			
	100.32				Ti^{+4}	2			
					Mn^{+2}	5			
					O^{-2}	2534			

Analyst E. P. Henderson. $Ca_{10}Mg_{46}Fe_{44}$ (atomic %)

* Al divided between four fold and six fold positions in proportions necessary to balance the excess electrical charge of the Fe^{+3} and Ti^{+4} ions in $X+Y$ group.

just as it is in terrestrial plutonics. But the cooling in its original environment did not proceed far enough to cause most of the pigeonite to invert to hypersthene though a small part of it, about 10 per cent, has inverted possibly after it became a meteorite.

Thus, to sum up, it is believed that six pyroxene solid phases were present at one time or another during the history of the meteorite, the relations between the four phases now visible can be explained, and their derivation from an original solid phase, pigeonite A, indicated.

PLAGIOCLASE

The plagioclase was analyzed by Henderson (Henderson and Davis, 1936) and found to be bytownite, $Or_{.5}Ab_{10.7}An_{88.8}$. It is clear, colorless

TABLE 4. OPTICAL PROPERTIES OF PYROXENE PHASES

	α	β	γ	Biref.	2V	Optic Plane	Dispersion	$Z\Lambda c$	Estimated Composition
Pigeonite B	1.7085	1.7095	1.736	.0275	+21°	$\perp\{010\}$	$r>v$	40°	$Ca_5Mg_{47.5}Fe_{47.5}$
Augite C	1.697	1.702	1.7255	.0285	+52°	$\parallel\{010\}$	$r>v$	44.5°	$Ca_{43}Ng_{36}Fe_{21}$
Hypersthene E	1.710	1.713	1.7255	.0155	−52°	$\parallel\{010\}$	$r<v$ strong	0°	$Mg_{49.5}Fe_{50.5}$
Salite F	1.688	approx.	1.715	—	—	—	—	—	$Ca_{50}Mg_{32}Fe_{18}$

and glassy in the crushed sample. Zoning is not observable though rarely small portions of a crystal appear to have suffered some late stage alteration to slightly less calcic plagioclase.

A remarkable feature is the almost total absence of visible cleavage in the thin section. The plagioclase does commonly contain curved, apparently conchoidal, fracture planes; in many cases these are dotted by minute blebs and tiny spherical particles of a metallic mineral. In the few cases where cleavage was noted it was on {001}. The {010} cleavage was not observed though a suggestion of {110} and {1$\bar{1}$0} parting was seen in one grain. The absence of cleavage will be commented on further in the consideration of the primordial environment.

The plagioclase has minute inclusions of a faintly pink, translucent mineral. It appears to be isotropic and has an index of refraction considerably lower than the feldspar but higher than the tridymite. Roughly it must be near 1.51. It has not been identified. The tiny opaque inclusions along fractures in the plagioclase (and to a lesser extent in the pyroxene) have already been mentioned. These range from distinctly visible blebs and tiny spherical masses to exceedingly minute specks. When viewed under the high power objective a transition can be seen from clearly identifiable specks to particles so small and closely spaced along the fracture surface that they trail out into a gray haze in which the individual particles are too small for the resolving power of the microscope. The fact that they have the form of droplets rather than crystals suggests that they may be metallic iron. Since they are in all cases found on fractures, they are clearly younger than the essential silicates.

The twinning observed in the plagioclase is rather unusual; pericline and albite twins predominate, with subordinate twinning on the manebach, ala A and ala B laws. Carlsbad twinning was not noted in any of the grains examined. For plagioclase of this composition some uncertainty exists in the identification of the twinning laws. At this composition it is very difficult to determine which is the plus and which the minus end of Z (N_γ) optical direction. This is occasioned by the fact that the poles of {010} and {001} are almost symmetrically disposed on either side of the plane containing X and Y. Thus there is some doubt in many cases as to whether a given twin pair represent manebach or albite, ala A or ala B, and Carlsbad or pericline, etc. A positive determination can be made in those cases where pericline twinning has occurred and the {001} cleavage, at a low angle to it, is observable. Table 5 below summarizes the observations made on the twinning but as pointed out above contains some uncertain determinations. Pericline twinning is more common in terrestrial bytownites and anorthites than in more sodic varieties, but it seems to be even more common in this meteorite than in terrestrial bytownites.

The number of twin lamellae is small in a given crystal. In general the bulk of the area of a crystal in this section consists of a single member or simple pair of twins. Within this large area are found fine, widely spaced, twin lamellae.

TABLE 5

No. of crystals	*Twinning laws*
10	albite, pericline
2	albite, pericline, manebach
1	albite, manebach
1	manebach, ala A, ala B
1	albite, ala B
1	albite, ala A
1	pericline

There is an obvious crystallographic orientation of the plagioclase which is no doubt a dimensional orientation. More than three quarters of the crystals examined have the pole of $\{100\}$ within 45° of the vertical. When considered in conjunction with the pyroxene *c* axis orientation, it may be concluded that the plagioclase crystals are tabular parallel to $\{100\}$, the *c* and *b* crystallographic axes are about of equal length but *a* is shorter.

TRIDYMITE

The tridymite occurs as anhedral grains interstitial to the pyroxene and plagioclase. It is evidently the last of the essential constituents to crystallize. It has very low birefringence and exhibits a patchy extinction under crossed nicols. The optical angle ranges from 45° to 50° and the indices of refraction are near 1.47. It is crowded with minute inclusions. These consist of sharp, well formed, acicular crystals, probably apatite, and the unidentified pinkish isotropic mineral, previously mentioned in the discussion of the plagioclase, and minute opaque specks.

OPAQUES

The opaque metallic grains were separated from the silicates magnetically and mounted in bakelite for study. Most of them are too small to make satisfactory determinations on them. The largest grains, about 0.15 mm., are of two varieties: one, an isotropic gray metallic mineral, occurring in equidimensional grains, probably chromite; two, a strongly anisotropic and pleochroic metallic having a purplish color which is probably an ilmenite-magnetite solid solution. Each grain consists of two or three polygonal crystals with sharp straight boundaries between them. No trace of exsolution lamellae are to be seen in these grains such as are always present in comparable terrestrial ilmenites. A third metallic constituent which occurs as rounded blebs, is bright white in reflected light and may be metallic iron. There is a general tendency for the larger opaque grains to lie on or near plagioclase-pyroxene boundaries.

TEXTURE AND FABRIC

The pyroxenes generally range from 2 to $2\frac{1}{2}$ mm. in length along the *c* axis and are $1\frac{1}{2}$ to $2\frac{1}{2}$ times as long in this direction as at right angles to this direction. The plagioclases commonly are 0.5 to 1.5 mm. and are nearly equidimensional in the plane of the one thin section studied.

In general appearance the relations between crystals is similar to that found in crystal accumulates such as the rocks of the Stillwater Complex, Bushveld Complex, Skaergaard Intrusion, etc. Boundaries of original euhedral crystals which collected on the floor of a magma chamber have been added to form the interstitial liquid thus filling the remaining space and adding irregularities on a small scale to the former euhedral outlines of the settled crystals. Against late stage minerals which crystallize entirely from pore space liquid, the original settled crystals present well formed crystal faces. Such is the case in this meteorite at contacts of plagioclase or pyroxene with tridymite. Growth along the borders of large pyroxene grains has included smaller plagioclases so that locally small areas of ophitic to subophitic texture result. This is illustrated in the photomicrograph, Fig. 1, and in the drawing, Fig. 3.

Rough petrofabric diagrams were made by examining 24 pyroxene and 17 plagioclase crystals on the universal stage. These are adequate to show a well defined fabric. In the case of the pyroxenes, the *c* axes form a girdle almost parallel to the plane of the thin section, Fig. 4. An area representing a small circle on the stereographic projection with a diameter of 90° contains only one pyroxene *c* axis. The center of this circle is about 15 degrees from the center of the projection, or in other words the fabric pattern makes an angle of this amount with the plane of the thin section. The plagioclases in the plane of thin section examined are almost equidimensional and show no obvious fabric until compared to a stereographic plot of the poles of crystal faces (following somewhat the same procedure as used by van der Berg, 1947). The plot, Fig. 5, shows a strong tendency for the poles of {100} faces to be nearly vertical to the plane of the section and for the poles of the zone [100] to be horizontal. This indicates that the crystal habit of the feldspars probably was such that growth along the *b* and *c* axes was considerably greater than along the *a* axis and the crystals therefore are tabular parallel roughly to {100}. They are so arranged in the fabric that the longer axes, *b* and *c*, lie in the same plane as the longest axis of the pyroxenes (the *c* axis). The conclusion which may be drawn from the whole fabric is that it is one of essentially planar dimensional orientation of the crystals. Secondarily there is an indication of a tendency toward a weak linear orientation of the longest axis of the pyroxenes in the plane of layering. Such a fabric as this is characteristic of crystal accumulates formed by settling of crystals to the floor of a magma chamber and accumulation there in nearly horizontal layers and probably could not have developed in any other manner. Thus evidence is found to indicate magmatic differentiation by crystal settling in an extra-terrestrial body.

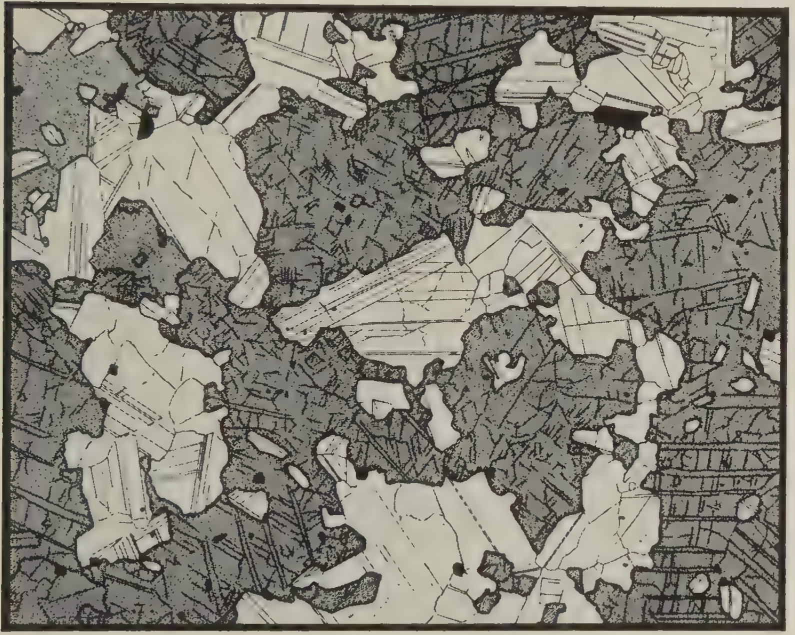

FIG. 3. Drawing of a portion of the thin section of the meteorite (traced from photograph). White = plagioclase; dotted = pyroxene, note augite lamellae parallel to {001} of pigeonite; black = opaque minerals; gray (two areas in upper left-hand corner) = tridymite. Long dimension of figure equals 1.2 centimeters. Opaque grains tend to lie along boundaries between plagioclase and pyroxene.

The tridymite plays a passive role in the fabric, having crystallized from pore space liquid after the fabric was formed.

Primordial Environment and Early History of the Meteorite

The texture and grain size of the meteorite and the complete absence of zoning in the plagioclases indicates that it crystallized very slowly probably from a large body of magma. The orientation of the crystals with their longer axes tending to lie in one plane but without pronounced linear orientation of the longest axes in that plane indicates a primary layering of the igneous rock from which it was derived. This type of layering cannot be attributed to primary flow structure or to later orientation during metamorphism but almost unquestionably is the result of the sedimentation of crystals on the original floor of the magma chamber as set forth by Peoples (1934) in the case of the Stillwater Complex (also see Buddington, 1934, Wager and Deer, 1939). From this it is deduced that magmatic differentiation by crystal sorting has taken place in an extra-terrestrial body.

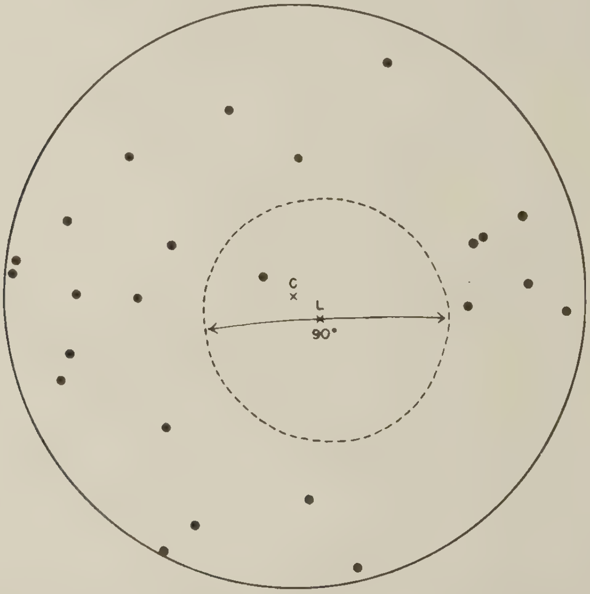

FIG. 4. Stereographic plot of the *c* axes of the pyroxenes with respect to the plane of the thin section. *C* is the center of the net and perpendicular to the thin section. *L* is the pole of the supposed plane of layering in the meteorite.

The temperature at which the meteorite crystallized must have been above the inversion temperature of the pyroxene (approximately 1065° C). Comparable rocks which have crystallized near the Earth's surface would have formed in the neighborhood of 1100° C. (Hess, 1941).

In the case of this meteorite there is no positive indication of the pressure conditions during its crystallization. Pressure could quite possibly raise the crystallization temperature to 1200° C.

The almost complete absence of cleavage in the plagioclase might well be a relic of its original high pressure environment. The occurrence of minute metallic inclusions along conchoidal fracture planes in the plagioclase rather than on cleavage planes also points to the lack of cleavage when it was in its original environment. The pyroxene, however, has well developed cleavage. This may have developed upon decrease of pressure after the rock became a meteorite. It is interesting to note that Daly (1938) suggested that cleavage in such minerals as pyroxene and plagioclase might not be present at pressures equivalent to 40 km. or more in the Earth.

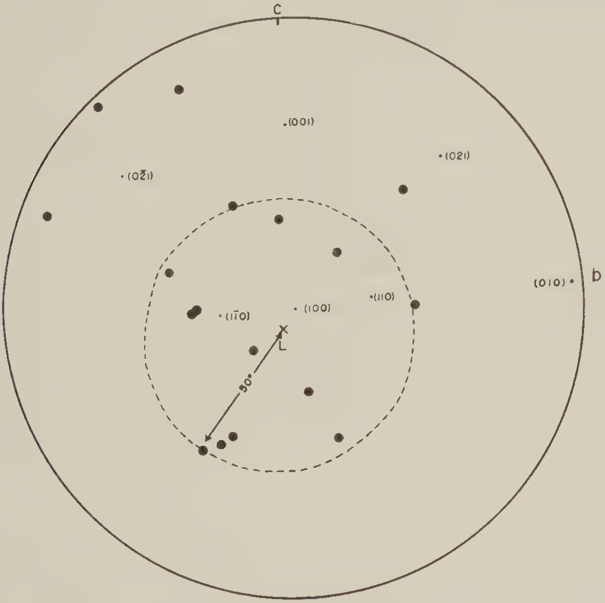

FIG. 5. Each dot represents the pole of the thin section with respect to the crystallographic orientation of a plagioclase crystal in the section. *L* as in Fig. 4 represents the supposed plane of layering. Note clustering of dots in the general vicinity of the pole of {100}. Had the plane of layering been exactly parallel to the plane of the section, the dots would have presumably been so disposed that the pole of {100} would have been at the center of the dashed circle.

After complete crystallization the normal temperature of the environment in which this meteorite existed must still have been above the inversion temperature for the pigeonite, 1065° C. This is comparable to temperatures thought to obtain in the deeper part of the Earth's crust. The composition of the meteorite is similar to the composition at such a level in the Earth's crust according to the postulates of Buddington (1943). The temperature of the meteorite's primordial environment might be placed at 1135° C. ± 65°.

There is a suggestion that the body from which the meteorite was derived was of relatively large size, that is, it could not have been as small as an asteroid and could more appropriately be considered as coming from a body having a size of the order of magnitude of the Earth. The gravity field must have been sufficient to produce settling of 1 mm. plagioclase crystals with a density only 0.05 greater than the magma.

The slow crystallization and the temperature level also place a lower limit on the probable size of the original body. The usual reasoning from meteorites to speculation as to the composition of the interior of the Earth might in this case be reversed. If our concepts concerning the interior of the Earth are approximately correct, it probably would take a very large body of the bulk composition of the Earth to segregate from it a crust of basaltic composition. Judging from some of Jeffreys' recent papers there appears to be a fairly good correlation between diameter and composition of the inner planets and their satellites. Thus if the hypothetical parent of the meteorites did not have a diameter similar to the Earth it would probably not have had a crust of basaltic composition as does the Earth. In recent papers on meteorites Patterson and Brown (1948) conclude that exceedingly high pressures would be required to account for some of the observed phase relations in meteorites so that a parent body comparable to the Earth in size is suggested.

The event which produced the separation of the meteorite from its environment must have been of sudden and catastrophic nature. The tridymite did not invert to quartz nor did the bulk of the pigeonite invert to the orthorhombic form. To preserve these forms requires sudden chilling.

GENERAL CONCLUSIONS

The conclusions which are summarized below are deductions the writers made from rather limited data as represented in single thin section of one small specimen and accompanying chemical analyses of the meteorite as a whole and its component essential minerals. Admittedly these conclusions are speculative as by the very nature of the materials, they must be. Their validity may some day be capable of stronger proof when more such meteorites are found and studied.

The Moore County meteorite possibly came from the deeper part of the crust of a planet comparable in size to the Earth. It is a product of crystallization of an intrusion of basaltic composition which appears to have differentiated by crystal settling to form a layered complex. The temperature conditions were in the neighborhood of 1135° C. The meteorite left this environment during catastrophic break up of the planet with great speed and consequent sudden cooling.

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ATTERBERG PLASTIC LIMITS OF CLAY MINERALS*

W. Arthur White†

Abstract

The Atterberg plastic limits of the common pure clay minerals are presented. The data obtained indicate that the plastic limit of attapulgite>montmorillonite>illite >kaolinite; that the liquid limit of sodium montmorillonite>calcium montmorillonite =attapulgite>illite>kaolinite; and that the plastic index of sodium montmorillonite>calcium montmorillonite>attapulgite>illite>kaolinite. The data show also that all the Atterberg limits increase with decreasing particle size.

Introduction

The purpose of this report is to present the Atterberg plastic limits of pure clay minerals and the effect of the particle size of the clay minerals on the Atterberg limits. Because clay minerals are dominant components of most clay materials (soils, shales, tills, loesses, and clays), which are aggregations of particles of one or more clay minerals and frequently such non-clay materials as quartz, feldspars, organic matter, etc., the data on pure clay minerals should be very useful in interpreting data for natural clay materials. The Atterberg limits are widely used, particularly by engineers, as a means of estimating the plastic properties of clay materials.

Acknowledgments

The author is deeply indebted to the late Professor T. T. Quirke of the University of Illinois for his valuable advice and suggestions and to Drs. M. M. Leighton, Chief, and R. E. Grim, Head of the Division of Clay Resources and Clay Mineral Technology, for use of the facilities of the Illinois State Geological Survey.

Definition

The Atterberg limits of a soil or clay are the liquid limit, plastic limit, and plastic index, and Allen[1] defines them as follows:

1. "Liquid limit is the moisture content, expressed as a percentage by weight of the oven-dry soil, at which the soil will just begin to flow when jarred slightly."

2. "Plastic limit is the lowest moisture content, expressed as a per-

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[1] Allen, Harold, Classification of soils and control procedures used in construction of embankments: *Public Roads*, **22,** 263–265 (1942).

centage by weight of the oven-dry soil, at which the soil can be rolled into threads $\frac{1}{8}$ inch in diameter without breaking into pieces. Soil which cannot be rolled into threads at any moisture content is considered non-plastic."

3. "Plastic index is the difference between the liquid limit and the plastic limit . . . It is the range of moisture content through which a soil is plastic. When the plastic limit is equal to or greater than the liquid limit the plastic index is recorded as zero."

PROCEDURE

The clay minerals, as determined by *x*-ray, differential thermal and microscopic analyses, were illites, kaolinites, montmorillonites, halloysites, attapulgite, and allophanes (Table 1).

The illites, the kaolinite from Union County, Illinois, and the montmorillonites from Mississippi were fractionated to less than 1.0 micron; also the illites (except the illite from Ohio) and the Union County kaolinite were fractionated to less than 0.5 micron. The remaining clays were not fractionated because they either would not disperse or they formed thixotropic suspensions.

The Atterberg limits were determined in accordance with Allen's[2] definition except that the liquid limit was determined in the Casagrande liquid limit machine as described by Casagrande.[3]

In determining the liquid and plastic limits of all the clay minerals except the montmorillonite from Belle Fourche, South Dakota, and attapulgite, the water was added to the clays until the plastic and liquid limits were reached.

The Belle Fourche montmorillonite, perhaps because it is the sodium type, requires different treatment because it forms a gel when water is *evenly* dispersed between the particles; whereas if water surrounds a lump, it will not penetrate to the interior because the outer surface will gel, forming an impermeable layer around the lump. It is, therefore, almost impossible to start with the dry clay and add water without forming lumps.

In order to get a smooth mixture of water and montmorillonite, the bentonite was added slowly to the water through a screen while the water was being stirred by a milk-shake machine. The montmorillonite was added until a gel was set up. This gel was stirred by moving the cup around the stirring blade to break up any lumps formed. The gel was

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[2] Allen, Harold, *op. cit.*

[3] Casagrande, Arthur, Research on the Atterberg limits of soils: *Public Roads,* **13,** 121–130 (1932).

TABLE 1. THE ATTERBERG LIMITS OF CLAY MINERALS

Clay	Particle Size Microns	Plastic Limit	Liquid Limit	Plastic Index
Illite				
1. Grundy Co., Illinois	whole	35.70	61.20	25.50
	<1.0	39.59	83.00	43.41
	0.5	52.27	103.65	51.38
2. LaSalle Co., Illinois	whole	24.75	35.90	11.15
	<1.0	46.21	85.55	39.34
	0.5	52.98	111.25	58.27
3. Vermilion Co., Illinois	whole	23.87	29.05	5.18
	<1.0	44.44	95.05	50.61
	0.5	44.90		
4. Jackson Co., Ohio	whole	28.77	53.95	25.18
	<1.0	35.16	61.25	26.09
Kaolinite				
5. Union Co., Illinois	whole	36.29	58.35	22.06
	<1.0	37.14	64.20	27.06
	0.5	39.29	71.60	32.31
6. Twiggs Co., Georgia	whole	29.86	34.98	5.12
Montmorillonite				
7. Belle Fourche, S. Dakota	whole	97.04	625–700	528–603
8. Pontotoc, Mississippi	whole	81.41	117.48	36.07
	<1.0	109.48	175.55	66.07
Attapulgite				
9. Quincy, Florida	whole	116.64	177.80	61.16
Halloysite				
10. Halloysite, Eureka, Utah		not plastic		
11. Hydrated halloysite, Lawrence Co., Indiana		not plastic		
Allophane				
12. Lawrence Co., Indiana		not plastic		

poured into a pan and allowed to dry in air, the contents being stirred every day to keep an even and smooth mixture. Data were recorded when the montmorillonite became rigid enough to take 10 taps on the liquid limit machine and were continued to 50 taps.

The attapulgite had a gelling property similar to that of the sodium type montmorillonite, but it was not so pronounced. The same procedure was used to obtain the liquid limit of attapulgite as was used with the Belle Fourche montmorillonite.

Discussion

From the data (Table 1), the illites showed that with decrease in particle size the Atterberg limits increase. The illites from La Salle and Grundy Counties, Illinois, showed excellent correlation between particle size and the Atterberg limits. The Atterberg limits for the illite from Vermilion County, Illinois, indicated that most of the minus 1.0μ particles were near 0.5μ; whereas those for the illite from Ohio suggested that the particles were for the most part near 1.0μ in the minus 1.0μ fraction. The low Atterberg limits for the whole samples from La Salle and Vermilion Counties showed the influence of non-clay impurities as determined with the microscope. The plastic limit for an illite clay would probably range from 25 to 55 per cent; the liquid limit, from 50 to 115 percent; and the plastic index, from 25 to 60 per cent, with the variations depending upon particle size.

The kaolinites were represented by a very fine crystalline kaolinite from Union County, Illinois, and a very coarse crystalline kaolinite from Georgia. About 70 per cent of the Union County kaolinite was less than 0.5μ and most of the Georgia kaolinite was about 2μ. The kaolinites also showed the effect of particle size on the Atterberg limits, but these variations are not as great as for the illites. The plastic limit of kaolinite would probably range from less than 25 to 40 per cent; the liquid limit from 30 to 75 per cent; and the plastic index from 0 to 35 per cent. The shrinkage of the kaolinite would be less than that of the illites.

The montmorillonites were of two types: one carrying sodium as the exchangeable base (Belle Fourche, South Dakota) and the other carrying calcium (Pontotoc, Mississippi). The plastic limits of the two were about the same, but there was a great difference in the liquid limits which was probably due to the nature of the exchangeable base. The sodium montmorillonite set up gels which increased the liquid limit and also caused the results to be somewhat erratic. The calcium montmorillonite had a plastic index little greater than that of illite, but the plastic and liquid limits were considerably higher. Klinefelter et al.[4] reported the plastic limit of montmorillonite as high as 250 per cent. The plastic range for this mineral would probably be 80 to 250 per cent; the liquid limit, from 115 to 700 per cent; and the plastic index, from 35 to 600+ per cent. This means that the montmorillonite upon drying would shrink considerably more than the illite.

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[4] Klinefelter, T. A., et al., Syllabus of Clay Testing, Part I, *U. S. Bur. Mines, Bull.* **451,** p. 7 (1943).

The Atterberg limits of attapulgite are closely similar to those of the calcium montmorillonite. The shrinkage would be greater than that of illite and would probably about equal that of calcium montmorillonite.

Both the Eureka, Utah, halloysite, which was the lower hydrated form, and the Indiana halloysite, which was the higher hydrated form of this mineral, were nonplastic. However, work in progress suggests that some of the halloysites ranging between these two extremes are plastic.

The allophanes are amorphous hydrous aluminum silicates. The two samples used in this experiment were not plastic. However, it is possible that amorphous clay materials may be found that are plastic.

Conclusions

The data obtained on the plastic clays would indicate that the Atterberg limits increase with decreasing particle size. It would also indicate that the plastic limit of attapulgite > montmorillonite > illite > kaolinite; that the liquid limit of sodium montmorillonite > calcium montmorillonite = attapulgite > illite > kaolinite; and that the plastic index of sodium montmorillonite > calcium montmorillonite > attapulgite > illite > kaolinite. The shrinkage would probably be montmorillonite > attapulgite > illite > kaolinite.

THE DUFRENITE PROBLEM*

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TABLE OF CONTENTS

Abstract.. 513
Introduction.. 514
Historical Survey... 514
Dufrenite... 516
  Crystallography... 517
  Physical Properties.. 518
  Chemical Composition... 519
  Sjögrenite... 521
Rockbridgeite.. 523
  Physical Properties.. 523
  Optical Properties of Rockbridgeite and Dufrenite.............................. 524
  Chemical Composition... 527
Isomorphous Substitution in Dufrenite and Rockbridgeite.......................... 529
Chemical Analyses of Dufrenite-Like Minerals of Uncertain Identity............... 530
Alteration of Dufrenite and Rockbridgeite.. 531
Unidentified Dufrenite-Like Minerals... 533
Laubmannite and Andrewsite... 534
Beraunite.. 536
Acknowledgments.. 539
References... 539

ABSTRACT

It is shown that several different basic iron phosphates have been confused since earliest times under the name dufrenite. The history and nomenclature of the subject is reviewed in detail. The specific name dufrenite is here re-defined to apply to a particular mineral of the dufrenite-complex, and the new name rockbridgeite is proposed for the other common member of this complex.

Both dufrenite proper and rockbridgeite are shown to be basic phosphates of ferrous and ferric iron that ordinarily are found in a more or less oxidized condition, analogous to vivianite. Dufrenite has the probable formula $Fe''Fe'''_4(PO_4)_3(OH)_5\cdot 2H_2O$ and while crystals are seemingly orthorhombic the substance is probably monoclinic. Hirschberg, Thuringia, may be taken as the type locality and seven other localities are described. Rockbridgeite has the probable formula $Fe''Fe'''_6(PO_4)_4(OH)_8$ and is monoclinic or triclinic. Midvale, Rockbridge County, Virginia, may be taken as the type locality and eight other localities are described. *X*-ray diffraction patterns, optical and physical properties and other characterizing data are given for both dufrenite and rockbridgeite. Dufrenite may be dimorphous with beraunite. Rockbridgeite may be isostructural with chenevixite but not with chalcosiderite. The earliest stage of alteration of dufrenite and rockbridgeite is marked by conversion of Fe'' to Fe''' with accompanying slight leaching of P_2O_5 but without any marked change in the *x*-ray diffraction pattern; this stage is followed by a more or

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 304.

less complete removal of P_2O_5 with the formation of hydrous iron oxide and the destruction of the crystal structure.

Laubmannite, a second new but rare species separated from the drufrenite-complex, has the formula $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$ and is isostructural with andrewsite, the copper analogue. Laubmannite occurs at Shady, Polk Co., Arkansas, and probably at the Nitzelbuch mine, Amberg district, Bavaria. Characterizing *x*-ray, optical and other data are given for this species and also for two other probably new but unnamed dufrenite-like minerals. Beraunite is shown to be, like dufrenite and rockbridgeite, a more or less oxidized basic ferrous-ferric phosphate and not a straight ferric phosphate as hitherto considered. A new occurrence of beraunite at Middletown, New Jersey, is described. Five new chemical analyses are reported, including one each of beraunite, laubmannite, and dufrenite and two of rockbridgeite. The reported analyses of other minerals in the dufrenite-complex that cannot definitely be shown to belong to either dufrenite or rockbridgeite are discussed.

An iron phosphate from Wheal Phoenix, Cornwall, described by Kinch and Butler to which the name sjögrenite was later applied by Krenner in the belief that it differed from other dufrenite-like minerals, is shown to be identical with ordinary dufrenite. Krenner almost certainly mistook chalcosiderite for Kinch and Butler's mineral, and the name sjögrenite should not be adopted in his meaning as urged by Quensel but be retained for the carbonate-hydroxide to which it is presently applied.

INTRODUCTION

Dufrenite is widespread in nature, but our knowledge of the mineral has been very unsatisfactory in all respects, particularly with regard to its crystallography and chemical composition. A survey of numerous Museum specimens labelled dufrenite and representing 17 different localities, many of them already described in the literature, has now revealed that several different basic iron phosphates have been confused under the name from earliest times. Two of these substances are almost equally common, and these together comprise the source material of most of the already published data relating to the supposedly single species dufrenite. It has not yet proven possible to achieve a complete description of any of these substances, however, and the purpose of the present paper is to draw attention to the problem and to record the data already at hand. A characterizing description of dufrenite proper, as here defined, and of the several dufrenite-like substances recognized during the course of the work is given on the following pages.

HISTORICAL SURVEY

The basic iron phosphate called dufrenite was first recognized as a distinct entity by Werner and other mineralogists of his time under the name *grüneisenerde*. Ullmann, writing in 1814, referred to the mineral as *grüneisenstein*, including both *strahlicher* and *ochrichter* varieties, and cited the Offhäuser and Mittelberg iron mines in the Hollerter Zug, Siegen, Westphalia, as the only localities known to him. *Fasrige*, *dichte*, *zerreibliche* and other physical varieties also were distinguished by other early writers, and there is little doubt but that several different minerals of similar appearance or constitution were confused with the true dufrenite. Chalcosiderite was separated from *grüneisenstein* by Ullmann in 1814. The mineral was thought at that time to be an iron oxide, and Haüy as late as 1822 referred to it as *fer oxidé, terreaux, jaune verdâtre.* The chemical composition of the mineral was first established by the analyses of Vauquelin in 1825 and of Karsten in 1827.

Vauquelin's mineral, not referred to by a specific name, came from a pegmatite at an unstated locality in Haute-Vienne, France. His analysis, cited beyond in Table 3, showed a very high content of MnO. A significant content of manganese is characteristic of dufrenite from pegmatites, where it ordinarily forms as an alteration of triphylite or other iron-manganese phosphates, but manganese is nearly or entirely lacking in dufrenite from iron-ore deposits, gossans or sedimentary formations. Our present knowledge of dufrenite is largely based on material from the latter types of occurrence and the mineral has been long accepted as essentially a phosphate of iron rather than of manganese. Vauquelin's material, in light of the new findings reported here, apparently corresponds to a manganese analogue of dufrenite. It seems advisable to retain the modern use of the name and apply it to an iron phosphate, or the iron-rich portion of an isomorphous series with a corresponding manganese-iron phosphate rather than to revise the established nomenclature. As will be seen, there are additional complications in the nomenclature of dufrenite, so-called, and this preliminary simplification of the problem is very desirable. An added justification for this suggestion is that there is some uncertainty as to the true identity of Vauquelin's mineral.

Karsten, who was unaware of the work of Vauquelin, gave in 1827 what can be considered to be the first definitive description of the substance later known as dufrenite. His material, referred to as *grüneisenstein*, came from an unstated locality in the Hollerter Zug at Siegen. Karsten's analysis, cited in Table 3, established the mineral as a hydrated phosphate of iron which approximated the formula $2Fe_2O_3 \cdot P_2O_5 \cdot 2\frac{1}{2}H_2O$, but it was remarked that this formula was uncertain because a significant although unknown amount of ferrous iron was present in the mineral. Nevertheless, most later workers have regarded the substance as a straight ferric compound, and the formulas $2Fe_2O_3 \cdot P_2O_5 \cdot 3H_2O$ and $5Fe_2O_3 \cdot 3P_2O_5 \cdot 8H_2O$, among others, have been proposed to represent the mineral.

A specific name, dufrénite, was first applied to the mineral in 1833 by Brongniart. According to P. A. Dufrénoy, after whom the mineral was named, Brongniart's specimens came from Hirschberg, Westphalia, and Anglar, Haute-Vienne, France. The Hirschberg locality, actually in

Thuringia, is on the Saale river about ten miles from Hof; and the locality Anglar, itself a mistake for Angelard, was confused by Dufrénoy with the occurrence of another mineral, angelardite (=vivianite), the true locality of Brongniart's mineral being Huréaux en Saint-Sylvestre in Haute-Vienne as shown by Lacroix. This probably is the locality of the specimens analyzed by Vauquelin. Some years later, in 1841, the name kraurite was proposed for the species by Breithaupt for lack of knowledge of Brongniart's name. This name is still used in preference to dufrenite in some German literature, although it clearly lacks priority.

DUFRENITE

It is here proposed, as a means of procedure, to select the earliest described occurrence of grüneisenstein that can be recognized as dufrenite, in the broad sense, and to arbitrarily establish it as dufrenite proper. Vauquelin's mineral is unsatisfactory for the purpose for reasons already indicated, aside from being unavailable, and the minerals of Karsten and of Brongniart must next be considered. Karsten's material would be ideal for the purpose if his original specimens were available. In lack of this material, recourse might be made to a specimen from exactly the same locality that his came from. Unfortunately, Karsten gave the locality only as the Hollerter Zug,[1] near Siegen, Westphalia, which includes at least several known localities for dufrenite. Two specimens of dufrenite from the Siegen area, one labelled simply Siegen, Westphalia, and the other as near Herdorf, Westphalia, were available to the writer. These specimens proved to be different. The former specimen, however, was identical with two specimens from the Hirschberg, Thuringia, locality named by Dufrénoy. It is here proposed to restrict the name dufrenite to this particular mineral. Specimens from the Huréaux locality of Dufrénoy were not available for study.

X-ray powder diffraction patterns afford the only certain means of distinguishing between the various dufrenite-like minerals. The *x*-ray powder pattern of dufrenite as here defined is given in Table 16. Identical patterns were afforded by material from seven other localities as listed in Table 1. These are at present the only proven localities for the mineral but doubtless others will be established from among the numerous localities for so-called dufrenite described in the literature.

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[1] A name given to a linear group of siderite veins extending for some miles near Siegen, and representing one of a number of named vein-systems in the central iron-ore district of Westphalia between Siegen and Altenkirchen. The Hollerter Zug is part of the larger Eiserfelder Gangzug. There are also individual iron mines named Hollertszug near Dermbach, at Offhausen and at Herdorf in the Daaden-Kirchen area of this district.

Crystallography. None of the specimens from the localities listed afforded suitable material for either morphological or single-crystal x-ray study. With the exception of the crystals from the Wheal Phoenix, described below, the mineral occurs as crusts and botryoidal masses with a divergent fibrous structure. X-ray rotation photographs taken about the direction of elongation of seemingly single fibers gave powder patterns with very broadly marked intensity maxima unsuited for the measurement of the fiber period and indicating a considerable departure from parallelism of the individual fibrils. The Wheal Phoenix mineral is composed of tablets grouped together in subparallel, sheaf-like aggregates that are surficially altered to limonite. Cleavage fragments are markedly composite and it proved impossible to obtain usable single-crystal x-ray photographs. Some of the specimens of this mineral apparently were unaltered on the surface because Miers, in a note appended to the paper by Kinch and Butler in which this mineral was first described, gave some approximate crystallographic measurements. Miers described the crystals as orthorhombic tablets flattened on $\{010\}$ and bevelled at the sides by small faces of $\{110\}$, $\{001\}$ and a rounded brachydome. His best measurements gave 86°26′ for the prism angle ($\phi = 46°47'$) and 12°45′ for the brachydome to the base. These measurements are fairly close to those obtained by Streng on relatively well developed crystals from the Rothläufchen mine, Waldgirmes, Hesse. Streng's crystallographic data, the best available for any of the dufrenite-like minerals, indicate his mineral to be orthorhombic. The crystals are cuboidal in habit with $\{100\}$, $\{010\}$ and $\{011\}$ as principal forms, the latter form more or less rounded, with small faces of $\{110\}$ and $\{120\}$. His measured angles, tabulated below,

TABLE 1. PROVEN LOCALITIES FOR DUFRENITE

Siegen, Westphalia. (Dark olive green to olive brown radial fibrous crusts with a botryoidal surface on limonite.)
Hirschberg, Thuringia. (Radial fibrous aggregates of olive brown to greenish black color in limonite and quartz. Here taken as the type locality.)
Wheal Phoenix, Cornwall. (Sub-parallel aggregates and crusts of rectangular plates on limonite. Also as dark greenish black botryoidal crusts with a radial fibrous structure on limonite.)
Hauptmannsgrün, near Reichenbach, Saxony. (Dark greenish black botryoidal crusts with a fibrous structure, on limonite.)
Ullersreuth, Saxony. (Dark greenish black to olive green botryoidal crusts with a fibrous structure on limonite.)
Leobenstein, Thuringia. (Olive brown to greenish black radial fibrous masses on limonite.)
Rock Run, Cherokee Co., Alabama. (Thick radial fibrous crusts on limonite. Color dark greenish black; luster brilliant.)
Rothläufchen mine, Waldgirmes, Hesse. (This material, described by Streng, is probably but not certainly identical with dufrenite.)

give the ratio 0.873:1:0.426. Neither Miers' nor Streng's observations, if the latter are relevant, are sufficiently good to definitely establish the symmetry as orthorhombic.

	ϕ	ρ
010	0°00′	90°00′
100	90°00′	90°00′
110	48°52′	90°00′
120	29°47′	90°00′
011	0°00′	23°05′

Physical Properties. Dufrenite ordinarily occurs as botryoidal masses or crusts with a radial fibrous structure. The surface of the crusts sometimes is drusy and composed of sub-parallel grouped crystals with rounded or exfoliated terminations. Distinct crystals, such as those from the Wheal Phoenix and from Waldgirmes, are rare. The color is dark green or olive green grading to greenish black. The mineral alters readily, first by more or less complete oxidation of the ferrous iron present with an accompanying change in color to shades of olive brown to reddish brown but with retention of other properties, and finally becomes brown or yellow-brown with an ochreous consistency. The hardness is 3½ to 4½. The values reported for the specific gravity of so-called dufrenite vary over a wide range, no doubt due to the fibrous character of the mineral and to variation in the degree of alteration. Some of the measurements reported in the literature can not be ascribed to a definite species. These include the values 3.500–3.555 of Ullmann, 3.4987–3.5609 of Karsten and 3.534 of Diesterweg on Hollerter Zug material, and the value 3.872 of Bořicky on material from St. Benigna, Bohemia. New determinations on the microbalance of material known definitely to belong either to dufrenite or rockbridgeite are given in Table 2 together with values reported in the

TABLE 2. SPECIFIC GRAVITY OF DUFRENITE AND ROCKBRIDGEITE

Locality	Dufrenite		Locality	Rockbridgeite	
	New	Lit.		New	Lit.
Siegen	3.29		Rockbridge	3.37	3.383 3.454
Hirschberg	3.33	3.227	Palermo	3.33	
Wheal Phoenix, fibrous		3.08	Fletcher	3.45	
Wheal Phoenix, crystals		3.233	Herdorf	3.40	
Ullersreuth	3.34		Hagendorf	3.38	
Alabama	3.34		Ullersreuth	3.33	

literature for material from the same localities. The most representative value for the species is probably 3.34. Bořicky's value, 3.872, is entirely out of line and either is in error or does not represent the minerals at hand. The optical properties of dufrenite are described and tabulated on a following page in connection with the description of rockbridgeite.

Chemical Composition. Chemical analyses are available for only three of the occurrences here established as belonging to dufrenite proper (Columns 3, 4, 5 in Table 3). These are of the fibrous and crystallized types of the mineral from the Wheal Phoenix, Cornwall, described by Kinch and by Kinch and Butler, respectively, and of the material from Rock Run, Alabama, analyzed by Wells.[2] Kinch derived the formula $Fe''Fe'''_6(PO_4)_4(OH)_8 \cdot 4H_2O$ from his analysis after deducting the CaO and MgO as impurities. If these cations are taken to be essential constituents, as seems likely, the ratio of $RO:R_2O_3$ becomes significantly higher than that expressed by the formula (1.28:6 instead of 1:6). Kinch and Butler's analysis differs from that of Kinch in that it entirely lacks FeO

TABLE 3. CHEMICAL ANALYSES OF DUFRENITE AND OF SOME RELATED MINERALS

	1.	2.	3.	4.	5.	6.
CaO			1.68	1.50		
MgO			0.17	tr.		
FeO			6.80		2.2	1.53
MnO	6.76					
Fe_2O_3	56.2	63.45	47.03	55.63	56.5	60.20
Al_2O_3			0.87			
P_2O_5	[27.84]	27.72	31.10	30.26	31.8	31.82
H_2O	9.2	8.56	11.47	10.62	9.1	8.03
Rem.			0.43	1.48	0.1	
Total	[100.00]	99.73	99.55	99.49	99.7	101.58
G			3.08	3.233		3.39

1. Huréaux (?), France. Vauquelin analysis. 2. Hollerter Zug, Westphalia. Karsten analysis. 3. Dufrenite, Wheal Phoenix, Cornwall. Fibrous type. Kinch analysis. Rem. is SiO_2. 4. Dufrenite, Wheal Phoenix. Crystals. Kinch analysis in Kinch and Butler. Rem. is SiO_2 0.53, CuO 0.95. 5. Dufrenite, Rock Run, Alabama. Wells analysis, 1939. Published by permission of the U. S. Geol. Survey. Rem. is SiO_2. 6. Dufrenite (?) Waldgirmes, Hesse. Streng analysis.

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[2] The writer is indebted to the U. S. Geological Survey for permission to use this hitherto unpublished analysis.

and nearly lacks other divalent cations that might substitute therefor. Since the two minerals are found by x-ray study to be structurally identical, it may be supposed that divalent iron was originally present in Kinch and Butler's material and was later oxidized to the ferric condition without accompanying structural changes of consequence. Wells' analysis of the Alabama material contains a small and irrational amount of FeO and also may be considered to be partly oxidized. On this assumption, all three analyses together with the analysis by Streng of the Waldgirmes mineral (which is apparently identical with true dufrenite on crystallographic grounds) may be arbitrarily calculated to a series of simple ratios between R_2O_3 and P_2O_5 with concomitant conversion of excess Fe_2O_3 to FeO. A selected set of relatively simple ratios calculated in this way is given in Table 4. The best formula for the mineral is taken as

$$Fe''Fe'''_4(PO_4)_3(OH)_5\cdot 2H_2O$$

Table 4. Some Calculated Ratios for Dufrenite Analyses

Analysis in Table 3	$RO : R_2O_3 : P_2O_5$			Calculated per cent		Ideal formula
				FeO	Fe_2O_3	
3. Kinch	1.28	3	2.17	Analysis ratio		
4. Kinch and Butler	0.90	3	2	4.09	51.08	$FeFe_6(PO_4)_4(OH)_8\cdot nH_2O$
5. Wells	0.63	3	2	5.04	53.34	
6. Streng	0.918	3	2	7.39	53.69	
3. Kinch	2.98	7	5.06	Analysis ratio		
4. Kinch and Butler	3.24	7	5	7.15	47.68	$Fe_3Fe_{14}(PO_4)_{10}(OH)_{18}\cdot nH_2O$
5. Wells	2.48	7	5	7.98	50.08	
6. Streng	3.30	7	5	10.63	50.09	
3. Kinch	2.06	4	3	8.37	45.29	
4. Kinch and Butler	2.34	4	3	8.19	45.41	$FeFe_4(PO_4)_3(OH)_5\cdot nH_2O$
5. Wells	1.88	4	3	10.12	47.70	
6. Streng	2.38	4	3	12.77	47.71	
3. Kinch	3.42	5	4	11.00	42.37	
4. Kinch and Butler	3.79	5	4	11.75	42.57	$Fe_2Fe_5(PO_4)_4(OH)_7\cdot nH_2O$
5. Wells	3.18	5	4	12.84	44.72	
6. Streng	3.84	5	4	13.93	44.72	

This formula is preferred over $Fe''Fe'''_6(PO_4)_4(OH)_8 \cdot H_2O$, which is just about as satisfactory on an oxide-ratio basis, because it brings Wells' analysis better into line and gives also very exact ratios for Kinch's analysis. As already pointed out, the latter analysis, if taken as correct, contains too much RO, even before any correction for partial oxidation, to fit a formula based on $R_2O_3:P_2O_5=3:2$. It might also be noted that several analyses high in RO of dufrenite-like minerals that have been reported in the literature but which can not be associated with any definite species, for lack of *x*-ray data, also conform to the formula given. These analyses are described in a following section. The mineral beraunite, discussed beyond, may have the same formula as dufrenite and thus be dimorphous with that species.

The above line of interpretation is also taken in the case of the new minerals rockbridgeite and laubmannite, described beyond. The interpretation of all of these minerals as more or less oxidized compounds of both ferrous and ferric iron, rather than as straight ferric compounds as done earlier, is also indicated by the following more general considerations:

(1) Ca and Mg are often present in small but significant amounts which do not yield any simple or systematic numerical relation to Fe''' or P. This suggests that these cations were originally present in substitution for another divalent cation, presumably Fe'', that has since been "lost" by oxidation.

(2) Ferrous iron itself is commonly present in small and irrational amounts, and in some analyses reaches an apparent maximum of roughly 8 weight per cent FeO. This circumstance suggests that the low values of FeO represent cases of partial oxidation. The situation thus would be somewhat similar to that obtaining with vivianite.

(3) Manganese is sometimes present in small, irrational amounts in the divalent but not trivalent state. The non-oxidation of manganese from Mn'' to Mn''', while the original Fe'' has at the same time gone over to Fe''', would reflect the higher oxidation potential of this element relative to iron, a fact exemplified in the oxidation of lithiophilite-triphylite.

(4) Laubmannite, a new basic ferrous-ferric phosphate described beyond, is isostructural with the mineral andrewsite which is a basic phosphate of ferric iron and divalent copper. Laubmannite, however, contains a large excess of ferric over ferrous iron, and a formula analogous to that of andrewsite with Fe'' equivalent to Cu'' is obtained only when some ferric iron is converted to ferrous as argued in the case of dufrenite.

(5) Rockbridgeite may be isostructural with chenevixite, a basic arsenate of ferric iron and divalent copper, and ferrous iron would be structurally equivalent with the copper. Rockbridgeite affords rational formulas only when treated analogously to dufrenite and laubmannite.

Sjögrenite. The specimen from the Wheal Phoenix described earlier is part of the type material of Kinch and Butler and is of particular interest because of a knotty problem in nomenclature connected therewith. The specimen itself was acquired by the Harvard Museum in 1943 from Mr. Hugh A. Ford, a mineral collector and dealer, who had obtained it directly from Mr. F. A. Butler with the assurance that it was one of the original specimens described by him and Kinch. Kinch and Butler had found that the mineral differed somewhat in composition from that often attributed to dufrenite ($2Fe_2O_3 \cdot P_2O_5 \cdot 3H_2O$), a matter already discussed, but referred to it as "dufrenite?" and did not propose a new name. The closing sentence of their paper reads "Having regard to the conclusions we have so far arrived at, it is not our intention to propose a new name for this mineral." In the 10th International Geological Congress, held in Stockholm in 1910, the Hungarian mineralogist J. A. Krenner gave an informal talk, recorded by the Secretary of the meeting, P. Quensel, in the Procès-Verbaux, in which it was stated that Kinch and Butler's material has a domatic cleavage, inclined extinction and is triclinic. No measurements are cited and no statement is made of the authenticity of the specimens. Krenner proposed the new name sjögrenite after the Swedish mineralogist Hjalmar Sjögren. Krenner's name did not receive notice in the abstracting journals and general reference works until it was mentioned, without reference, thirty years later in Klockmann-Ramdohr's *Lehrbuch* (1942) and Strunz's *Tabellen* (1941). These works were not available in the United States until 1945 because of the war. In 1941, the present writer, unaware of Krenner's remarks and finding no prior use of sjögrenite proposed this name for a new member of the hydrotalcite group. In 1945, Quensel published a note drawing attention to the matter and urged retention of the name for the Wheal Phoenix mineral. The present study, however, proves that Kinch and Butler's mineral is identical with minerals earlier described as dufrenite including what is here considered to be the type material. In view of this, the writer would prefer to see the name sjögrenite preserved as a species designation for the carbonate-hydroxide mentioned rather than relegate it to the synonymy of dufrenite.

Krenner's statements definitely indicate that he examined chalcosiderite instead of dufrenite. Chalcosiderite has domatic cleavage, inclined extinction and is triclinic, in accordance with Krenner's description, and occurs not only at Wheal Phoenix but on some at least of the type specimens of the Wheal Phoenix dufrenite. Kinch and Butler do not specifically mention chalcosiderite as being present although this is inferred by their statement " . . . the evidence of certain specimens in the possession of the authors points pretty conclusively to the occasional origin of brilliantly crystallized chalcosiderite in the decomposition of this phosphate [dufrenite]." The writer's specimen of Kinch and Butler's material, however, contains chalcosiderite associated with the dufrenite; and a specimen labeled dufrenite from Wheal Phoenix in the Yale collection (Brush No. 975) consists entirely of chalcosiderite. The Wheal Phoenix dufrenite, as originally described, and confirmed here, has parallel extinction, no signs of domatic cleavage and morphologically appears to be orthorhombic. The writer feels that these facts alone are sufficient to invalidate the name sjögrenite as applied to a dufrenite-like mineral.

ROCKBRIDGEITE

About half of the specimens labelled "dufrenite" examined in the course of the present study were found to give an x-ray powder pattern entirely distinct from that of dufrenite proper. The powder pattern data are given in Table 16. This mineral is indistinguishable from dufrenite in its general appearance and has been confused with that species since earliest times. Material from four of the nine localities here recorded in Table 5 for this new species have already been described by others under the name dufrenite. These include the well-known occurrence in Rockbridge County, Virginia, here taken as the type occurrence because of the wide distribution of this material in collections.[3]

TABLE 5. PROVEN LOCALITIES FOR ROCKBRIDGEITE

Midvale, Rockbridge Co., Virginia. (Dark greenish black, compact fibrous masses. With limonite.)
Greenbelt, Maryland. (Dark greenish black to black radial fibrous crusts with a brilliant luster lining cavities in limonite concretions.)
Polk County, Arkansas. (Greenish brown to olive green radial fibrous crusts with limonite.)
Palermo mine, North Groton, New Hampshire. (Radial fibrous crusts and masses altering from triphylite in pegmatite. Color greenish black to olive green, bronze-brown, reddish brown.)
Fletcher mine, North Groton, New Hampshire. (Greenish black coarse radial fibrous masses as an alteration of triphylite in pegmatite.)
Near Herdorf, Westphalia. (Yellow brown to olive brown radial fibrous crusts on limonite.)
Kreuzberg, near Pleystein, Bavaria. (Greenish black fibrous masses as an alteration of triphylite in pegmatite.)
Hagendorf, Bavaria. (Radial fibrous masses of a dark olive green color as an alteration of triphylite in pegmatite.)
Ullersreuth, Saxony. (Radial fibrous masses of a dark brown to olive brown color in limonite.)

Physical Properties. Rockbridgeite is identical in appearance with the fibrous varieties of dufrenite. The mineral forms fibrous crusts and masses ranging from small-botryoidal shapes with a radial structure to thick crusts with a straight or sub-parallel fibrous or fine-columnar structure. Concentric color banding is sometimes observed in these aggregates, as in dufrenite. No single-crystals of the mineral have yet been found, and the aggregate character of the fibers is such as to prevent single-crystal *x*-ray study. Rockbridgeite is very similar chemically to dufrenite. Material in which the ferrous iron is more or less oxidized to ferric becomes dark reddish brown in color but the luster and hardness remain unimpaired. On further alteration the color turns brown or yellowish brown and the material becomes soft and ochreous as described beyond. The hardness is $3\frac{1}{2}$–$4\frac{1}{2}$. The specific gravities newly determined here or earlier reported are cited in Table 2. The values vary considerably due to the fibrous nature of the material and to variation in composition and in alteration. The best value for the essentially pure iron compound is probably 3.45. The specific gravity of rockbridgeite probably is slightly higher than that of dufrenite, as are the indices of refraction.

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[3] The original material came from the outcroppings of a limonite deposit on South Mountain about one mile east of Midvale and ten miles east of Lexington in the Blue Ridge Mountains, Rockbridge County, Virginia. The specimens are ordinarily found labelled only Rockbridge County, Virginia. Several tons of the mineral are said to have been mined for distribution among collectors and dealers.

Optical Properties of Rockbridgeite and Dufrenite. The optical properties of these minerals as newly measured are listed in Tables 6 and 7. Optical data given earlier by Larsen and later summarized by Larsen and Berman for so-called dufrenite are given in Table 8; it is not certain to which species these data actually refer.

TABLE 6. OPTICAL PROPERTIES OF DUFRENITE (NEW DATA)

	Rock Run	Wheal Phoenix (crystals)	Hirschberg	Hirschberg	Siegen	Wheal Phoenix (fibrous)
*n*X	1.820	1.837	1.832	1.845	1.842	1.810
*n*Y	1.830	1.845	1.837	1.855	1.850	1.813, varies
*n*Z	1.925	1.895	1.890	1.890	1.875	1.855
Pleochroism						
X	deep blue	pale yellow brown	deep bluish green	pale yellow brown	pale brown	pale yellow brown
Y	buff	pale brown to olive brown	pale yellow brown	yellow brown	brown	deep blue
Z	deep red brown, olive brown	dark brown, red brown	deep olive brown	dark brown, olive brown	dark brown	deep greenish blue
Absorption	Z>X>Y	Z>Y>X	Z>X>Y	Z>Y>X	Z>Y>X	Z>Y>X
Opt. sign	+	+	+	+	+	+
2V	small	small	very small	mod.	small	small to mod.
Dispersion	$r<v$	$r>v$	$r<v$	$r<v$	$r<v$	$r>v$

The optical characters of both rockbridgeite and dufrenite vary widely and are of little value for diagnostic purposes. Both minerals are marked by extreme dispersion, crossed, and show abnormal green, orange, red or ultrablue interference colors without sharp extinction in white light. The axial dispersion is usually $r<v$, but sometimes is $r>v$, and always is extreme. The pleochroism of both minerals is marked. Z is always the most strongly absorbed and X, less frequently Y, the least strongly absorbed direction. The absorption colors vary widely. Material with much divalent metal present, either Fe″ or Mn″ or both, shows intense blue, bluish green or olive-green absorption colors for Y and Z, with X yellowish brown. Oxidized material with little or no divalent metal lacks the blue to green tints and shows reddish brown, brown or olive-brown tints for Y and Z and pale yellow brown for X. The absorption may be so intense, even in small grains, to make accurate measurement of the indices or extinction angles impossible. The absorption becomes less marked as the extent of oxidation of Fe″ to Fe‴ increases. Under the microscope, both dufrenite and rockbridgeite show one perfect cleavage with another less perfectly developed, both usually parallel to the fiber length, and sometimes traces of a third cleavage approximately at right angles to the other two. The vibration direction Z always is perpendicular to the best cleavage; either X or Y is parallel to the elongation. Dufrenite in some instances shows parallel extinction against cleavage lines in the plane of the best cleavage, taken as {010},

TABLE 7. OPTICAL PROPERTIES OF ROCKBRIDGEITE (NEW DATA)

	Fletcher mine, N. H.	Rockbridge Co., Va.	Palermo mine, N. H.	Ullers-reuth	Herdorf	Polk Co. Ark.
*n*X	1.875	1.873	1.875	1.847	1.914	1.838
*n*Y	1.880	1.880	1.890	varies	varies	varies
*n*Z	1.897	1.895	1.920	1.945	1.935	1.915
Pleochroism						
X	pale brown	pale yellow brown	pale yellow brown	pale yellow brown	pale brown	pale yellow brown
Y	bluish green	bluish green	pale olive green	brown	brown	yellow brown to olive brown
Z	dark bluish green	dark bluish green	dark olive green	dark brown	dark brown	brown to olive brown
Absorption	Z>Y>X	Z>Y>X	Z>X>Y	Z>Y>X	Z>Y>X	Z>Y>X
Opt. sign	+	+		+, mostly		
2V	mod.	mod.	mod. to large	mostly small	mostly mod.	mostly mod.
Dispersion	$r<v$			$r<v$, mostly		$r>v$, mostly

and such plates when turned on edge show sharp parallel extinction. Some finely fibrous dufrenite, notably that from Siegen, shows extinction angles measured from the elongation up to 30° probably due to the subparallel or twisted aggregation[4] of the fibers. The crossed dispersion indicates that dufrenite is monoclinic or triclinic although the morphological evidence and parallel extinction previously mentioned indicates orthorhombic symmetry. Relatively perfect cleavage laths and fibers of rockbridgeite show definite extinction angles of about 3° to Y, together with

Table 8. Optical Properties of "Dufrenite" from Larsen (1921)

		Saxony		Ullersreuth	
	Type A	Type B	Type C	Type A	Type C
nX	1.830	1.830	1.840	1.840	
nY	1.840	1.840		1.845	
nZ	1.885	1.885		1.89	
Pleochroism					
X	bright green[a]	bright green	light yellow brown	pale yellowish	pale yellowish
Y	pale yellowish	pale yellowish	dark brown	dark reddish brown[b]	grass green
Z	dark reddish brown	dark reddish brown		dark reddish brown, dark green	
Absorption	Z>X>Y	Z>X>Y		Z>Y>X	
Opt. sign	+	−	+	+	+
2V	med. to large	large	small to large	varies; large	small
Dispersion	$r>v$	$r<v$	$r<v$	$r<v$	$r<v$
⊥ cleavage	Z	Z	Z	Z	Z
‖ elongation	Y	X	X	Y	X

[a] Brownish when 2V is small.
[b] Bright green when 2V is small.

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[4] A helicoidal type of aggregation in fibrous "dufrenite" from Rochefort-en-Terre, France, has been described by Lacroix.

crossed dispersion, and this substance apparently is monoclinic or triclinic.

The indices of refraction of both dufrenite and rockbridgeite vary widely. Rockbridgeite has in general higher values for the indices although both nX and nZ in single instances overlap the values for dufrenite. The birefringence seemingly varies markedly, ranging between 0.105 and 0.033 in dufrenite and between 0.098 and 0.024 in rockbridgeite. The values of the indices of refraction also vary markedly independently of the birefringence. It seems likely that both types of variation are due to varying degrees of oxidation or hydration of the material; the variation in birefringence may then be due to variation in these regards among different grains of a single sample. The indices of refraction given in Tables 6 and 7 were determined statistically so that the values for nX and nZ do not necessarily represent measurements on single grains and hence may not afford a measure of the true birefringence. The divergent optical character of the fibrous unaltered dufrenite from Wheal Phoenix and the thoroughly altered rockbridgeite from Herdorf is particularly interesting. Increasing oxidation of Fe'' to Fe''' apparently is accompanied by an increase in the values for the indices, especially nZ. Increasing hydration presumably has an opposite effect.

Chemical Composition. Four analyses are available for material known definitely to belong to the present species. These comprise two old analyses by Massie and by Campbell on what is termed the type material from Rockbridge County, Virginia, and two new analyses on material from Polk County, Arkansas, and the Palermo mine, New Hampshire, by Hallowell and Gonyer, respectively. The interpretation of these analyses presents a problem identical with that met with in dufrenite. The Palermo and Arkansas minerals contain small and irrational amounts of divalent cations, and the ferrous iron originally present is presumed to have been partially oxidized; the Rockbridge mineral may be essentially unaltered. The four analyses are cited in Table 9. These analyses as recalculated to some simple whole number ratios of R_2O_3 to P_2O_5, with accompanying conversion of excess Fe_2O_3 to FeO, are cited in Table 10. The most representative formula is probably:

$$Fe''Fe'''_6(PO_4)_4(OH)_8.$$

This formula meets the analysis ratios of the Rockbridge and the Arkansas material fairly closely. The fact that the two analyses of the Rockbridge material were made on separate samples and yet are in good agreement indicates that this material is unaltered. If this is so, the formula given is to be preferred over that based on a ratio of $R_2O_3:P_2O_5 = 4:3$, which requires a considerable conversion of Fe_2O_3 to FeO and

TABLE 9. CHEMICAL ANALYSES OF ROCKBRIDGEITE

	1.	2.	3.	4.
CaO	1.124			tr.
MgO	0.762	2.16		tr.
FeO	6.144	6.06	0.99	2.66
MnO	0.403	0.24	2.24	2.84
Fe_2O_3	50.845	50.89	55.84	55.00
Al_2O_3	0.212	0.29		tr.
P_2O_5	31.761	31.66	32.86	30.43
H_2O	8.531	8.35	7.96	8.06
Rem.	0.115	0.20		[1.01]
Total	99.897	99.85	99.89	[100.00]
G	3.382	3.454	3.33	

1. Rockbridge Co.. Va. Campbell analysis. Rem. is insol. 2. Rockbridge Co., Va. Massie analysis. Rem. is SiO_2. 3. Palermo mine, N. H. Gonyer analysis, 1948. 4. Polk Co., Ark. Hallowell analysis, 1948. Rem. not determined but largely SiO_2.

which also brings the Hallowell analysis out of line. The preferred formula, nevertheless, is unsatisfactory in that it is relatively high in divalent metals and in total metals relative to phosphorus and, further, the analysis of the Palermo mineral is widely divergent therefrom. The Palermo mineral conforms very closely to $Fe''Fe'''_7(PO_4)_5(OH)_8$.

The formula cited would make rockbridgeite the ferrous iron ana-

TABLE 10. SOME CALCULATED RATIOS FOR ROCKBRIDGEITE ANALYSES

Analysis in Table	RO : R_2O_3 : P_2O_5			Calculated per cent		Ideal formula
				FeO	Fe_2O_3	
1. Campbell	1.22	3	2.09	Analysis ratio		$FeFe_6(PO_4)_4(OH)_8 \cdot nH_2O$
2. Massie	1.32	3	2.08	Analysis ratio		
3. Gonyer	0.43	3	2	1.34	55.45	
4. Hallowell	1.14	3	2	5.94	41.36	
1. Campbell	3.24	7	5	7.19	49.68	$Fe_3Fe_{14}(PO_4)_{10}(OH)_{18} \cdot nH_2O$
2. Massie	3.55	7	5	7.35	49.45	
3. Gonyer	2.08	7	5	4.67	51.75	
4. Hallowell	3.86	7	5	9.01	47.94	
1. Campbell	2.33	4	3	9.33	47.30	$FeFe_4(PO_4)_3(OH)_5 \cdot nH_2O$
2. Massie	2.55	4	3	9.54	47.03	
3. Gonyer	1.65	4	3	6.88	49.29	
4. Hallowell	2.71	4	3	11.07	45.66	

logue of chalcosiderite, $Cu''Fe'''_6(PO_4)_4(OH)_8 \cdot 4H_2O$, disregarding uncertainties as to the water content of the former mineral. The two species are not isostructural, however, since their *x*-ray powder photographs are totally unlike and their physical and crystallographic characters are also unlike. The *x*-ray pattern of rockbridgeite, on the other hand, resembles that of chenevixite and these two species may be isostructural. The formulae derived from the three available analyses of this mineral, however, are inconsistent both with each other and with rockbridgeite as seen from the accompanying tabulation.

$Fe''Fe'''_6(PO_4)_4(OH)_8$	(rockbridgeite)
$Cu''Fe'''_6(PO_4)_4(OH)_8 \cdot 4H_2O$	(chalcosiderite)
$Cu''_5Fe'''_6(AsO_4)_6(OH)_{10} \cdot 8H_2O$	(chenevixite, New South Wales)
$Cu''_9Fe'''_{10}(AsO_4)_8(OH)_{24} \cdot 2H_2O$	(chenevixite, Tintic)
$Cu''_5Fe_4'''(AsO_4)_4(OH)_{10} \cdot 6H_2O$	(chenevixite, Cornwall)

It might also be considered that dufrenite and rockbridgeite are nonstoichiometric defect structures, but such an interpretation would be very speculative in lack of knowledge of the unit cell dimensions or crystal structure. The analyses themselves in most instances are probably not sufficiently accurate to permit more than an approximate formulation of the substances at best.

ISOMORPHOUS SUBSTITUTION IN DUFRENITE AND ROCKBRIDGEITE

The principal types of compositional variation in dufrenite and rockbridgeite are in the relative proportions of the divalent metals Fe, Mn, Ca, Mg and Cu, and in the proportions of Al and Fe'''. Significant amounts of Mn'' have not been reported in dufrenite, although an analysis by Schaller of an unidentified dufrenite-like mineral from Grafton, N. H., described beyond, may represent the manganese analogue of dufrenite. Vauquelin's old analysis (Table 3) of a brown fibrous manganese mineral from Huréaux (?) also might belong here. Both Ca and Cu'' substitute for Fe'' in dufrenite, with $Ca:Fe'' = 1:3.8$ in the fibrous material from Wheal Phoenix and $Cu:Fe'' = 1:10$ in the crystals from the same locality. It may be noted in this connection that laubmannite, $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$, described beyond, is isostructural and probably isomorphous with the copper analogue, andrewsite,

$$Cu''_3Fe'''_6(PO_4)_4(OH)_{12}.$$

Manganese is often present in rockbridgeite and a series extends up to at least $Mn'':Fe'' = 1:2$ in the Arkansas mineral analyzed by Hallowell. A significant amount of manganese also is present in the rockbridgeite from Palermo (Table 9) and in the unanalyzed material from the Fletcher mine; the rockbridgeite at both localities occurs as an alteration of triphylite in pegmatite. The unit cell dimensions as seen in x-ray powder photographs vary measurably with variation in the $Mn'':Fe''$ ratio, decreasing with increase in content of iron, and there also appears to be a slight variation in dimensions accompanying the oxidation of Fe'' to Fe'''. Aluminum may substitute for Fe''' in these minerals. A dufrenite-like mineral from Dandarragan, Western Australia, probably identical with true dufrenite and described in more detail beyond, has $Al:Fe'''=1:5.8$. An aluminian "dufrenite" from Rochefort-en-Terre, France, with 4.50 per cent Al_2O_3 has been analyzed by Pisani. Both dufrenite and rockbridgeite might well form a series to material with $Al>Fe'''$, analogous to the chalcosiderite-turquoise series. Trivalent manganese possibly also may substitute for ferric iron.

CHEMICAL ANALYSES OF DUFRENITE-LIKE MINERALS OF UNCERTAIN IDENTITY

At least 22 chemical analyses of dufrenite-like minerals have been reported in the literature. Most of these lack divalent iron. It has proven possible to associate some of these analyses with either dufrenite or rockbridgeite, as earlier discussed, but the others remain of uncertain affiliation. A few of the latter, however, contain relatively large amounts of divalent metals and hence are of particular interest in connection with the problem of formulation of these minerals. These analyses are described below.

A mineral from Grafton, New Hampshire, analyzed by Schaller (Column 1, Table 11) and labelled "near dufrenite" affords ratios agreeing almost exactly with the formula $(Mn, Fe, Ca)Fe'''_4(PO_4)_3(OH)_5 \cdot 1\frac{1}{2}H_2O$. This formula is identical with that proposed for dufrenite except that Mn'' and not Fe'' is the dominant divalent metal. The mineral hence would be the manganese analogue of dufrenite and entitled to species rank in its own right. It is not known, unfortunately, whether this mineral actually is isostructural with dufrenite; physical data are lacking, and the specimen itself has been lost.[5]

A so-called dufrenite described by Simpson from Dandarragan, Western Australia, is of interest because of its unusually high content of FeO and its bright green color, suggesting that it is essentially unoxidized. The analysis of this material (Column 2, Table 11) again conforms rather closely to the formula, $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2H_2O$, earlier proposed for dufrenite. The calculated ratios are $RO:R_2O_3:P_2O_5=1.78:4.02:3$, indicating a slight deficiency of divalent metals. The mineral occurs at Dandarragan as the petrifying substance of conifer-like wood fragments embedded in a ferruginous sandstone associated with beds containing phosphatic coprolites.

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[5] W. T. Schaller, private communication, 1948.

The highest content of FeO found in a dufrenite-like mineral is that reported by Schnabel in material from the Hollerter Zug. A physical description of the mineral was not given. The analysis (Column 3, Table 11) does not afford a rational formula, and in fact contains too little P_2O_5 to yield ratios close to those of dufrenite or rockbridgeite. The analysis probably is erroneous, particularly in view of the high summation and non-determination of divalent metals other than Fe.

Another mineral from Grafton, New Hampshire, analyzed by Schaller and labelled "near dufrenite" may be mentioned here. The analysis (Column 4, Table 11) conforms approximately to the formula $(Ca, Fe, Mg)Fe'''_2(PO_4)_2(OH)_2 \cdot 2H_2O$. This formula differs entirely from those of other dufrenite-like minerals, both in content of CaO and in ratios, but is close to that of some mitridatite and to xanthoxenite. The specimen has been lost[5] and confirmatory tests cannot be made.

TABLE 11. SELECTED ANALYSES OF UNIDENTIFIED DUFRENITE-LIKE MINERALS

	1.	2.	3.	4.
CaO	0.99	0.64		5.71
MgO	0.12			3.48
MnO	5.51	0.20		0.45
FeO	3.69	8.34	9.97	6.98
Fe_2O_3	47.44	40.15	53.66	39.77
Al_2O_3		4.44		
P_2O_5	31.87	31.26	28.39	32.40
H_2O	10.31	14.39	8.97	11.53
Rem.		1.12		
Total	99.93	100.54	100.99	100.32

1. Grafton, N. H. Schaller analysis of material labelled "near dufrenite." 2. "Dufrenite," Dandarragan, Western Australia. Bowley analysis in Simpson. Rem. is CO_2 0.24, SiO_2 0.48, C 0.40. 3. "Dufrenite," Hollerter Zug. Schnabel analysis in Rammelsberg. 4. Grafton, N. H. Schaller analysis of material labelled "near dufrenite."

ALTERATION OF DUFRENITE AND ROCKBRIDGEITE

Both dufrenite and rockbridgeite alter readily, a fact early noted by Karsten for the material from the Hollerter Zug. Karsten showed the final product to consist principally of hydrated iron oxide with 2.45 per cent P_2O_5 in brown material and 1.98 per cent in yellow material. Later, Diesterweg made a more detailed chemical study of the alteration sequence of the Hollerter Zug material. His analyses, cited in Table 12, show that even the earliest stage of the alteration, from the original green to the reddish brown state, is marked by a slight loss of P_2O_5; *x*-ray study by the writer of similar material shows no discernible structural change accompanying the alteration. Diesterweg's analysis of the yellow end product shows a P_2O_5 content of about one-fourth that originally present. Laubmann also has contributed data on the alteration of "dufrenite" from Auerbach, Bavaria. His analyses (Table 12) again show a marked leaching of P_2O_5 increasing with the extent of alteration. Observations on the alteration of "dufrenite" from St. Benigna, Bohemia, have been reported by Bořicky. Finally, the writer has examined the soft, yellow alteration crusts with a pseudomorphous fibrous structure often present on the rockbridgeite from Rockbridge, Virginia. The analysis of this material, cited in Table 12, shows a large reduction in P_2O_5 but little change in the content of H_2O. The ratios of the analysis are very close to $Fe'''_5(PO_4)(OH)_{12}$, if the very small amount of RO is disregarded, but this is fortuitous since *x*-ray study shows that the substance is a gross mixture of an unidentified mineral with goethite. Under the microscope, the former mineral appears as non-pleochroic shreds and fibers with a yellow color and indices between 1.87 and 1.93.

TABLE 12. ANALYSES OF ALTERED "DUFRENITE" AND ROCKBRIDGEITE

	1.	2.	3.	4.	5.	6.	7.
Fe_2O_3	62.02	59.14	80.03	65.85	78.38	73.58	52.73
P_2O_5	27.71	25.20	6.25	20.11	5.66	13.69	15.90
H_2O	10.90	13.98	14.06	13.61	14.20	10.32	23.15
Rem.		2.33		0.78	1.70	2.56	7.31
Total	100.63	100.65	100.34	100.35	99.94	100.15	99.09

1. Hollerter Zug, Westphalia. Green material. Diesterweg analysis. 2. Hollerter Zug. Reddish material. Diesterweg analysis. Rem. is Mn_2O_3. 3. Hollerter Zug. Yellow material. Diesterweg analysis. 4. Auerbach, Bavaria. Greenish white. Hiller analysis in Laubmann. Rem. is insol. 0.20, FeO 0.58. 5. Auerbach, Bavaria. Brown end product. Hiller analysis in Laubmann. Rem. is insol. 0.37, FeO 1.33. 6. Rockbridge, Co., Va. Yellow-brown alteration product of rockbridgeite. Hallowell analysis, 1947. Rem. is CaO 0.55, MnO 0.26, Al_2O_3 1.75. 7. Azovskite. Taman Peninsula. Efremov analysis. Rem. is CaO 2.84, SiO_2 2.64, CO_2 0.15, MgO tr., Mn_2O_3 1.68. H_2O includes $H_2O-11.28$, $H_2O+11.87$.

In accordance with the above observations on natural material, it has been found that artificially prepared ferric phosphate is slowly decomposed with continuous removal of phosphate when washed with water or with solutions containing organic matter, alkalies or certain salts. The voluminous literature in this field has been summarized by Mellor.

Some of the difficulties encountered in interpreting the analyses of dufrenite and rockbridgeite might be attributed to a leaching of phosphate from the material in its natural state. It seems probable that the decomposition is initially a surface effect, and proceeds thereafter at an advancing interface, in which iron phosphate is hydrolyzed leaving hydrous iron oxide and yielding phosphate ion to the solution. The material would then consist of two phases, hydrous iron oxide and unaltered mineral in varying degree of admixture depending on the extent of attack. Alternately, it may be supposed that the process of leaching is akin to base exchange, in which (PO_4) is diffused and lost without destruction of the crystal structure. The crystal chemistry of the process is not obvious. The analyses of dufrenite and rockbridgeite can be recalculated on these bases by progressively adding P_2O_5, or deducting Fe_2O_3, until simple ratios are obtained between $R_2O_3:P_2O_5$ or $RO:R_2O_3:P_2O_5$. It proves impossible, however, in the case of both dufrenite and rockbridgeite to fit the analyses simultaneously to a single, simple formula.

The oxidation of the iron from the divalent to the trivalent state may perhaps be compensated electrostatically by the disruption of OH groups and loss of H from the structure, as recently suggested by A. N. Winchell for some basic compounds of divalent iron. In this mechanism, there is no gain or loss of oxygen and, since packing requirements and coordination would be maintained, a considerable change in the structure would not be expected. This mechanism has been found by Barnes to operate reversibly when hornblende is heated in air or in hydrogen.

A basic ferric phosphate which, if a valid species, might occur as an intermediate stage in the alteration of dufrenite or rockbridgeite has been described by Efremov under the name azovskite. This material occurs as dark brown, metacolloidal masses and veinlets in sedimentary iron ores on the Taman Peninsula, Sea of Azov, USSR. The analysis, cited in column 7 of Table 12, approximates the formula $Fe'''_3(PO_4)(OH)_6$, probably fortuitously. The material may be a hardened gel-mass of coprecipitated hydrous iron phosphate and hydrous iron oxide. It shows weak birefringence, perhaps due to strain, with a mean refractive index of about 1.758.

UNIDENTIFIED DUFRENITE-LIKE MINERALS

Several unidentified minerals that resembled dufrenite were encountered in the course of the study. The best defined of these comprised a substance forming radial fibrous crusts and botryoidal masses with a pure black color and dark olive green streak. Luster vitreous, shining. Hardness 4 to $4\frac{1}{2}$. Specific gravity 3.51. Optically, the mineral is biaxial positive (+) with $nX \sim 1.82$ (deep blue), $nY \sim 1.83$ (olive brown) and

$nZ\sim1.88$ (very deep blue-green). There is one good cleavage, with Z perpendicular thereto, and another cleavage parallel to the elongation. The extinction angle of Y to the elongation is about 6°. Thick grains are nearly opaque. The dispersion is strong. This substance was found sparingly associated with reddingite in specimens from pegmatite at two localities, Hagendorf, Bavaria, and Vianua do Castelo, Maxedo, Portugal. The Hagendorf material is quite distinct from the rockbridgeite which occurs at this locality. The substance apparently is a basic phosphate of iron and manganese and is almost certainly a new species, but it is considered inadvisable to propose a new name in lack of a chemical analysis. The x-ray powder data for this mineral are listed in Table 16.

Another unidentified dufrenite-like mineral was found on a specimen from the Rothläufchen mine, Waldgirmes, Hesse. This is the locality from which Streng described the crystals of dufrenite (?) earlier discussed in connection with that species. The material comprises radial-fibrous crusts with a grayish green to yellow brown color and concentric color banding. The hardness is $4\frac{1}{2}$ and the specific gravity 3.23. Optically, the mineral is biaxial positive with $nX=1.850$ (yellow to yellow brown), $nY=1.855$ (yellow brown to olive brown), $nZ=1.875$ (yellow brown to reddish brown and olive brown). The pleochroism is weak, in contrast to dufrenite and rockbridgeite. The dispersion is strong, and 2V is moderate. The extinction against the fiber length is nearly or quite parallel. The x-ray powder pattern, poor in quality, is listed in Table 14. It differs from those of dufrenite and rockbridgeite but resembles that of the black mineral from Hagendorf and Maxedo described above. One wonders if this substance represents Streng's mineral, is an altered form thereof, or is a separate species.

Laubmannite and Andrewsite

A specimen labelled dufrenite, from Shady, Polk County, Arkansas, was found to give an x-ray powder pattern identical with that of andrewsite. The latter species was described in 1871 by Maskelyne from the West Phoenix mine, Cornwall, England.[6] An analysis by Flight, cited in Table 13, approximates to the formula $(Cu, Fe)_3Fe'''_6(PO_4)_4(OH)_{12}$ with $Fe'':Cu=1:1.4$. Andrewsite occurs as green to bluish green botryoidal masses with a radial fibrous structure on limonitic vein material. Two authentic specimens were available for examination. Optically, the mineral has $nX\sim1.813$ (pale yellowish green), $nY\sim1.820$ (emerald green) and $nZ\sim1.830$ (yellow to olive green). The dispersion is extreme, crossed, with $r<v$, and anomalous interference colors without sharp extinction are obtained in white light. The axial angle is moderate to large.

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[6] The locality is given simply as Cornwall in the original description but Collins in his account of henwoodite says that this species is found at the West Phoenix mine [near Liskeard] associated with andrewsite.

The dufrenite-like mineral from Arkansas occurs as thick crusts with a parallel-fibrous structure upon limonite. The inner parts are brown inclining toward dark brown and greenish brown in color with concentric color banding. Hardness $3\frac{1}{2}$ to 4, and specific gravity 3.33. The outermost parts of some of the crusts are somewhat altered, with a yellowish brown to grayish green color and reduced hardness. The optical properties are somewhat variable. The inner, fresh material is biaxial positive, with $nX=1.840$ (pale buff), $nY=1.847$ (greenish brown to olive green) and $nZ=1.892$ (reddish brown to olive brown). Absorption $Z>Y>X$. The dispersion is extreme, crossed, with $r<v$. 2V is variable but usually moderate. Crushed grains show one and perhaps two cleavages parallel to the fiber length. The x-ray powder patterns of this mineral and of andrewsite are listed in Table 16.

Table 13. Chemical Analyses of Andrewsite and Laubmannite

	1.	2.	3.	4.	5.
CuO	10.86	10.86	0.00	0.00	
CaO	0.09	0.09	1.14	1.14	
FeO	7.11	8.58	2.07	15.47	19.74
MnO	0.60	0.60	2.40	2.40	
Fe_2O_3	44.64	43.01	57.88	42.99	44.95
Al_2O_3	0.92	0.92	0.05	0.05	
P_2O_5	26.09	26.09	25.95	25.95	26.21
H_2O-			0.44	0.44	0.67
	8.79	8.79			
H_2O+			10.06	10.06	8.40
SiO_2	0.49	0.49			
Total	99.59	99.43	100.00	98.51	99.97
G	3.475		3.33		

1. Andrewsite, Cornwall. Flight analysis. $RO:R_2O_3=0.85:1$. 2. Andrewsite. Analysis 1 recalculated after converting enough Fe_2O_3 to FeO to make $RO:R_2O_3=1:1$. 3. Laubmannite, Shady, Polk Co., Arkansas. Hallowell analysis, 1948. Recalculated to 100 after deducting quartz from original sum of 100.14. With MgO 0.01. 4. Laubmannite. Analysis 3 recalculated after converting enough Fe_2O_3 to FeO to make $RO:R_2O_3=1:1$. With MgO 0.01. 5. Laubmannite (?) Nitzelbuch mine, Bavaria. Spengel analysis in Laubmann. $RO:R_2O_3:P_2O_5=2.98:3.04:2$.

A chemical analysis of the Arkansas mineral is cited in Table 13. Copper is entirely lacking, and there are not sufficient amounts of other divalent metals in its place to give the ratio $RO:R_2O_3=3:3$ indicated by the isostructural relation to andrewsite. The analysis as it stands affords

$RO:R_2O_3:P_2O_5 = 1:4.37:2.20$. It is considered that the mineral in its unoxidized state was the ferrous iron analogue of andrewsite and that most of the ferrous iron later oxidized to ferric. If enough Fe_2O_3 is converted to FeO to make $RO:R_2O_3 = 3:3$, the analysis appears as in column 4 of Table 13 and affords the simple ratio $RO:R_2O_3:P_2O_5 = 2.95:2.95:2$. The formula then is analogous to andrewsite:

Andrewsite	$(Cu, Fe, Mn)_3(Fe, Al)_6(PO_4)_4(OH)_{12}$
Laubmannite	$(Fe, Mn, Ca)_3Fe_6(PO_4)_4(OH)_{12}$.

The observed water content is slightly higher than that required by the formula, due probably to the fibrous nature of the material. As in the case of dufrenite and rockbridgeite, the oxidation of the iron from ferrous to ferric is apparently not accompanied by any structural changes discernible on an *x*-ray powder photograph. The name laubmannite is proposed for the species after the German mineralogist Heinrich Laubmann, who has made numerous contributions to the knowledge of the iron phosphates.

A mineral described by Laubmann in 1923 from the Nitzelbuch mine, Amberg-Auerbach district, Bavaria, may be identical with laubmannite in its unoxidized state. The mineral forms broad, radial fibrous bands and reniform crusts in limonite. Color dark green, with a very fresh appearance. Under the microscope the substance is said to have all the characters of "dufrenite." An analysis of the mineral by Spengel is cited in column 5 of Table 13. The ratios of the analysis yield the formula $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$ as found for the Arkansas mineral.

BERAUNITE

Beraunite is close to both dufrenite and rockbridgeite in composition, and its fibrous varieties resemble the reddish brown types of these minerals. Several specimens of beraunite were found erroneously labelled dufrenite. One of these, from Middletown, New Jersey, comprised discoidal concretions with a radial fibrous structure. The *x*-ray powder pattern and optical properties of this material were identical with those of beraunite from St. Benigna, Bohemia, and Eiserhausen, Nassau. A chemical analysis of the Middletown material is cited in Table 14. The analysis is of considerable interest because it reveals a small but significant

TABLE 14. CHEMICAL ANALYSIS OF MIDDLETOWN BERAUNITE

FeO	Fe_2O_3	Al_2O_3	P_2O_5	H_2O	Total	G
1.92	54.41	0.02	30.17	13.45	99.97	3.08

Hallowell analysis, 1948. Recalculated to original sum after deducting SiO_2 1.13 per cent.

content of ferrous iron, not hitherto reported in beraunite, that cannot be accommodated in any rational formula. This suggests that beraunite, like dufrenite and rockbridgeite, is properly a basic phosphate of both divalent and trivalent iron that is known ordinarily only in an oxidized condition. If the FeO is converted into Fe_2O_3, that is, oxidized, it is found that the ratios of the analysis then yield almost exactly the simple formula $Fe'''_5(PO_4)_3(OH)_6 \cdot 2H_2O$. This formula is identical with that derived from the three analyses of beraunite from St. Benigna reported by Tschermak and by Bořicky, aside from a slight deficiency in water. Since the Middletown material as presently constituted must be presumed to be the result of partial oxidation, a rational formula containing divalent iron must be sought for the original compound. A number of such formulae can be derived arbitrarily, depending only on the rational distribution of the available iron between FeO and Fe_2O_3, and no definite choice can be made between them. Since the amount of FeO present is likely to be small, the formulae $Fe''Fe'''_9(PO_4)_6(OH)_{11} \cdot 5H_2O$, with 5.03 per cent FeO, or $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 3H_2O$, with 10.06 per cent FeO, seem the more probable. The original analysis and weight per cent composition of the several formulae mentioned above are compared in Table 15. The formula last mentioned above is identical with that proposed for dufrenite, aside from a slight apparent difference in water content, and the two species may be dimorphous.

TABLE 15. PERCENTAGE COMPOSITION OF VARIOUS BERAUNITE FORMULAE

	1.	2.	3.	4.
Fe	39.51	39.74	40.22	39.56
P	13.15	13.22	13.39	13.17
H	1.50	1.51	1.45	1.51
O	45.84	45.53	44.94	45.75
	100.00	100.00	100.00	100.00

1. $Fe'''_5(PO_4)_3(OH)_6 \cdot 2\frac{1}{4}H_2O$.
2. $Fe''Fe'''_9(PO_4)_6(OH)_{11} \cdot 5H_2O$.
3. $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2\frac{1}{2}H_2O$.
4. Analysis of Middletown beraunite.

The Middletown beraunite has a reddish brown color in bulk with a concentric color banding in shades of dark greenish brown. The streak is brownish yellow with a tinge of olive drab. The luster is vitreous and brilliant, inclining toward resinous on cross-fractures. The hardness is 3 to $3\frac{1}{2}$, and the specific gravity is 3.08. Optically, the mineral is biaxial

TABLE 16. X-RAY POWDER DATA FOR DUFRENITE, ROCKBRIDGEITE AND SOME RELATED MINERALS

(Iron radiation (λ=1.937 Å), manganese filter. Low *d* values have been omitted in some instances)

Dufrenite		Rockbridgeite		Laubmannite		Andrewsite		Beraunite		Maxedo unknown		Waldgirmes unknown	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
12.33	3	8.41	1	12.14	2	5.98	1	10.32	10	7.00	2	9.61	1
6.90	1	6.90	2	5.04	5	5.52	1	9.60	1	4.86	3	7.97	3
6.54	1	4.83	1	4.38	2	5.01	5	7.20	3	4.66	3	6.97	3
6.10	1	4.64	1	4.12	3	4.54	1	4.80	4	4.37	1	6.41	1
5.59	1	4.34	1	3.81	1	4.35	2	4.39	2	4.21	1	5.20	5
5.05	9	4.19	1	3.63	1	4.16	3	4.09	1	3.59	2	4.84	1
4.84	1	3.58	3	3.40	5	4.02	1	3.73	2	3.40	10	4.15	1
4.40	3	3.43	1	3.22	10	3.78	2	3.41	5	3.19	10	3.71	6
4.15	4	3.37	2	3.18	10	3.55	1	3.28	1	3.02	1	3.46	8
4.04	1	3.18	10	3.01	4	3.42	3	3.18	3	2.93	½	3.30	2
3.79	1	3.02	3	2.88	4	3.22	10	3.06	8	2.76	2	3.18	10
3.67	2	2.94	1	2.64	2	3.19	3	2.82	1	2.68	1	3.03	2
3.54	1	2.85	1	2.44	3	3.01	3	2.72	3	2.59	2	2.80	3
3.42	9	2.76	3	2.11	6	2.89	3	2.56	3	2.42	8	2.76	1
3.24	8	2.67	2	2.06	2	2.79	1	2.48	1	2.34	½	2.59	3
3.17	10	2.59	3	2.01	2	2.65	2	2.41	1	2.27	1	2.44	5
3.01	4	2.42	5	1.96	1	2.60	1	2.31	2	2.18	1	2.30	1
2.88	5	2.33	1	1.73	3	2.50	1	2.22	1	2.15	1	2.13	1
2.81	2	2.26	2	1.61	2	2.44	5	2.10	2	2.11	2	2.07	2
2.64	3	2.23	1	1.58	3	2.34	1	2.06	1	2.07	1	1.97	1
2.58	2	2.16	1	1.53	1	2.24	1	1.99	2	2.03	1	1.92	1
2.50	1	2.11	1	1.49	1	2.17	2	1.97	1	1.97	3	1.87	1
2.44	5	2.06	3			2.12	8	1.92	4	1.92	1	1.84	1
2.38	1	2.02	2			2.07	1	1.87	1	1.90	1	1.75	1
2.29	2	1.96	3			2.02	2	1.81	1	1.86	1	1.71	3
2.23	2	1.94	1			1.96	2	1.79	1	1.83	2	1.62	5
2.16	1	1.90	2			1.87	1	1.74	1	1.80	1	1.58	1
2.11	6	1.84	3			1.83	1	1.71	1	1.74	1	1.55	2
2.07	4	1.80	1			1.76	1	1.70	1	1.72	1	1.53	1
2.02	1	1.75	1			1.73	4	1.67	1	1.71	1	1.47	1
2.00	1	1.71	1			1.69	2	1.65	1	1.68	1	1.41	1
1.95	3	1.69	2			1.67	2	1.61	3	1.64	2	1.29	3
1.92	1	1.64	2			1.62	5	1.59	1	1.61	2	1.16	1
1.86	1	1.59	8			1.59	4	1.56	1	1.59	4	1.14	1
1.83	1	1.55	1			1.54	1	1.53	1	1.56	1		
1.81	1	1.53	3			1.51	2	1.51	1	1.54	1		
1.77	1	1.51	1			1.49	1	1.49	1	1.51	1		
1.75	2	1.48	1			1.48	1	1.45	1	1.48	1		
1.73	3	1.46	1			1.46	2	1.32	1	1.46	2		
1.70	1	1.39	1			1.37	3	1.28	1	1.43	1		
1.68	2	1.29	3			1.34	3						
1.66	3	1.26	2			1.32	1						
1.63	2	1.24	1			1.29	2						
1.62	3	1.15	2			1.28	2						

positive with $nX=1.775$ (very pale yellow), $nZ=1.820$ (reddish to carnelian brown) and large 2V. The *x*-ray powder data are listed in Table 16.

Thermal Analyses of Beraunite, Rockbridgeite and Dufrenite. Satisfactory thermal analyses by the differential thermocouple method, using an Esterline-Angus recorder, could not be obtained. The best data indicate that the Middletown beraunite has an exothermic break peaking at about 625° C. and weak endothermic breaks peaking at about 220° and 340°. Rockbridgeite has an exothermic break near 650°, a weak endothermic break near 350° and possibly others. Dufrenite gave particularly bad records; an endothermic break is present at about 270° and other breaks are probably present. All three minerals begin to melt below 900°.

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FRONDELITE AND THE FRONDELITE-ROCKBRIDGEITE SERIES[1]

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ABSTRACT

The name frondelite is given to the mineral of composition $Mn''Fe_4'''(PO_4)_3(OH)_5$, isostructural and isomorphous with rockbridgeite, the ferrous iron analogue. The type locality of frondelite is the Sapucaia pegmatite, Municipio of Conselheiro Pena, Minas Gerais, Brazil, where it occurs in association with triphylite and other iron-manganese phosphates. It occurs in brown botryoidal masses with a radiating fibrous structure. It is orthorhombic with cleavages (100) excellent; (010) good; (001) fair. Hardness 4.5; sp. gr. 3.476; $\alpha=1.86$, $\beta=1.88$, $\gamma=1.893$; absorption in shades of orange $Z>Y>X$; 2V medium; dispersion $r>v$, strong. Orthorhombic, tentative space group $B22_1$ or $B22_12$ (D_2^5); $a_0=13.89$, $b_0=17.01$, $c_0=5.21$ Å.

The frondelite-rockbridgeite series is represented by frondelite, $Mn''Fe_4'''(PO_4)_3(OH)_5$ from the Sapucaia pegmatite, Brazil, manganoan rockbridgeite $(Fe''Mn'')Fe_4'''(PO_4)_3(OH)_5$, from the Fletcher quarry, North Groton, New Hampshire, and rockbridgeite $Fe''Fe_4'''(PO_4)_3(OH)_5$ from Rockbridge County, Va. Ferrous iron may oxidize to ferric iron. At Fletcher quarry green rockbridgeite $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ oxidizes readily to brown rockbridgeite, $(Fe''', Mn'')Fe_4'''(PO_4)_3(OH)_5$.

The variation of unit cell and optical properties are discussed. Three new analyses are given.

INTRODUCTION

In the summer of 1947 it was the privilege of the author to examine some phosphate minerals collected in 1945 by William T. Pecora of the U. S. Geological Survey from the Sapucaia pegmatite, Municipio of Conselheiro Pena, Minas Gerais, Brazil. One of these, a dark-brown, radially fibrous mineral occurring as crusts, botryoidal and drusy masses, appeared to resemble minerals previously grouped together as dufrenite. Dr. Clifford Frondel was at that time studying the dufrenite group, and kindly permitted use of his type material as standards for identification purposes. The mineral was found to be isostructural with rockbridgeite, $Fe''Fe_4'''(PO_4)_3(OH)_5$, now being described by Clifford Frondel. A chemical analysis showed the fibrous mineral to be the manganous end member, and the name frondelite is proposed for the mineral of composition $Mn''Fe_4''(PO_4)_3(OH)_5$. Frondelite is found in association with other iron-manganese pegmatite phosphates: triphylite, vivianite, and a member of the heterosite-purpurite series. The Sapucaia pegmatite and its minerals will be described in a forthcoming paper by W. T. Pecora and others.

PHYSICAL AND OPTICAL PROPERTIES

Frondelite from the Sapucaia pegmatite, Brazil, occurs as crusts and as botryoidal and drusy masses, showing in cross section a radiating fibrous structure. The fibers are parallel to the *c* crystallographic direction. Frondelite is orthorhombic; (100) is an excellent cleavage, (010) good, and (001) fair. The hardness is $4\frac{1}{2}$, the specific gravity 3.476. The luster is dull to vitreous. It is brittle, with an uneven fracture.

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[1] Published by permission of the Director, U. S. Geological Survey.

In the frondelite-rockbridgeite series frondelite is brown; rockbridgeite green. An intermediate member, manganoan rockbridgeite from the Fletcher quarry, North Groton, New Hampshire, is green where fresh, but readily oxidizes to brown radiating fibers. Rockbridgeite from Chanteloube, France, is brown in color. All known members of the series occur as radiating fibers.

Table 1. Optical Properties of the Frondelite-Rockbridgeite Series

	Unoxidized			Oxidized
	Frondelite (7.74 MnO, no FeO) Sepucaia Pegmatite (Lindberg)	Rockbridgeite (5.51 FeO, 3.73 MnO) Fletcher Quarry, N. H. (Frondel)	Rockbridgeite (6.14 FeO, 0.40 MnO) Rockbridge County, Va. (Frondel)	Rockbridgeite (MnO 4.10, no FeO) Fletcher Quarry, N. H. (Lindberg)
Indices				
α	1.860	1.875	1.873	1.915
β	1.880	1.880	1.880	1.927
γ	1.893	1.897	1.895	1.939
Pleochroism				
X	pale yellow brown	pale yellow brown	pale brown	pale yellow brown
Y	orange brown	bluish green	bluish green	orange brown
Z	orange brown	dark bluish green	dark bluish green	orange brown
Absorption	Z>Y>X	Z>Y>X	Z>Y>X	Z>Y>X
Optic sign	negative	positive	positive	
2V	moderate	moderate	moderate	large
Dispersion	$r>v$	$r<v$		$r>v$, if positive
Orientation				
X	$=c$			
Extinction	parallel			

The optical properties for rockbridgeite and frondelite are summarized in Table 1. The indices of refraction of frondelite were determined upon a small homogeneous fraction which was representative of the bulk of the larger sample. A small portion of the bulk sample may have been partly oxidized (as is substantiated by chemical analysis); a few grains gave values of γ as high as 1.93, and correspondingly high α and β.

Most grains show parallel extinction; a false extinction angle was noted by Frondel,[2] which was probably due to the radiating character of the material.

Table 1 clearly shows that the differences in indices of refraction between frondelite and rockbridgeite are not as large as the differences between green unoxidized and brown oxidized rockbridgeite that occur together at Fletcher quarry, North Groton, New Hampshire.

Rockbridgeite from Chanteloube, France, has variable indices of refraction; the lowest index for α observed was 1.865; the highest index for γ observed was 1.895. The sample is probably largely unoxidized, although some portions of the sample are very much altered. The MnO content is 3.53 per cent.

CHEMICAL COMPOSITION

In Table 2 are given the chemical analyses and ratios of various members of the frondelite-rockbridgeite series. Columns 1 through 4 give the

TABLE 2. CHEMICAL ANALYSES OF THE FRONDELITE-ROCKBRIDGEITE SERIES

	1	2	3	4	5		6		7	
					Analysis	Ratios	Analysis	Ratios	Analysis	Ratios
FeO	6.144	6.06	0.99	2.66	5.51	.0767	none		none	
MnO	0.403	0.24	2.24	2.84	3.73	.0526	4.10	.0578	7.74	.1091
MgO	0.762	2.16		trace	0.25	.0062	trace		0.20	.0050
CaO	1.124			trace	none		none		0.02	.0004
ZnO					0.16	.0020	0.16	.0020		
Na_2O					0.24	.0039	0.23	.0037	0.98	.0158
K_2O					trace		trace		0.12	.0013
Fe_2O_3	50.845	50.89	55.84	55.00	50.31	.3150	55.20	.3457	48.85	.3058
Mn_2O_3					none		0.32	.0020	1.75	.0122
Al_2O_3	0.212	0.29		trace	0.24	.0024	0.35	.0034	1.31	.0128
P_2O_5	31.761	31.66	32.86	30.43	32.43	.2284	31.67	.2231	31.28	.2203
H_2O	8.531	8.35	7.96	8.06	7.42	.4119	6.98	.3875	7.52	.4174
Rem.	0.115	0.20		(1.01)	0.07		0.16		0.32	
Total	99.987	99.85	99.89	100.00	100.36		99.17		100.09	
Sp. Gr.					3.474		3.490		3.476	

1. Rockbridge County, Va. Campbell analyst. Rem. is insol. On dufrenite from Rockbridge County, Va. J. L. Campbell, *Am. J. Sci.*, 3rd Series, 22, 65 (1881).
2. Rockbridge County, Va. Massie analyst. Rem. is SiO_2. On the composition of dufrenite from Rockbridge County, Va. F. A. Massie, *Chemical News*, 42, 181 (1880).
3. Palermo, N. H. Gonyer analyst. The dufrenite problem. Clifford Frondel, *Amercian Mineralogist*, **34,** 528.
4. Polk County, Arkansas. Hallowell analyst. Rem. not determined but largely SiO_2. The dufrenite problem. Clifford Frondel, *American Mineralogist*, **34,** 528.
5. Fletcher quarry, North Groton, N. H. Lindberg analyst. Unoxidized. Rem. insol.
6. Fletcher quarry, North Groton, N. H. Lindberg analyst. Oxidized. Rem. insol.
7. Frondelite, type locality. Sapucaia pegmatite, Brazil. Lindberg analyst. Rem. insol. Spectrographic analysis by K. J. Murata showed in addition .OX% Li, Be, Zn.

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[2] Frondel, Clifford, The dufrenite problem: *Am. Mineral.*, **34,** 524 (1949).

analyses of members of the rockbridgeite series, as reported by Frondel.[3] Columns 5 and 6 represent new chemical analyses of fresh and oxidized rockbridgeite from Fletcher quarry. In column 7 are given data for frondelite from the Sapucaia pegmatite, Brazil.

The molecular weight of the unit cell of frondelite may be derived from the formula,

$$M = \frac{\text{Vol. (in A}^3\text{)} \times \text{density}}{1.6604}.$$

The volume of frondelite, as derived from *x*-ray studies, discussed later in this paper, is 1231 Å^3. The molecular weight of the unit cell is 2577. In Table 3, column 4, the number of atoms of each kind per unit cell is found by multiplying the ratios from Table 2 by 0.01 to convert from a per cent to a fraction scale, and then multiplying by 2577. The formula so derived is $4\text{Mn}''\text{Fe}_4'''(\text{PO}_4)_3(\text{OH})_5$, which also fits the requirement of a minimum of four molecules per unit cell imposed by the space groups $B22_1$ or $B22_12$.

TABLE 3. FORMULA OF FRONDELITE

	Frondelite, Sapucaia Pegmatite					Rockbridgeite, Fletcher Quarry					
						Unoxidized			Oxidized		
	Ratios	Oxygen equivalent	Metal equivalent	Atoms per cell		Ratios	Atoms per cell		Ratios	Atoms per cell	
FeO						.0767	1.94	3.74			
MnO	.1091	.1091	.1091	2.812	3.83	.0526	1.33		.0578	1.47	1.70+1.80=3.51
MgO	.0050	.0050	.0050	.129		.0062	0.16		—		
CaO	.0004	.0004	.0004	.010		—	—		—		
ZnO						.0020	0.05		.0020	.05	
Na_2O	.0158	.0158	.0316	.814		.0039	0.20		.0037	.19	
K_2O	.0013	.0013	.0026	.067		—			—		
Fe_2O_3	.3058	.9174	.6116	15.761	17.05	.3150	15.94	16.06	.3457	17.53	17.80−1.80=16
Mn_2O_3	.0122	.0366	.0244	.629		—	—		.0020	.10	
Al_2O_3	.0128	.0384	.0256	.660		.0024	.12		.0034	.17	
P_2O_5	.2203	1.1050	.4406	11.354	11.35	.2284	11.56	11.56	.2231	11.31	11.31
H_2O	.4174	.4174	.8348	21.508	21.51	.4119	20.85	20.85	.3875	19.65	19.65

The ratios derived for frondelite show a small deficiency of R'', suggesting the possibility that some R''' may occupy positions equivalent to R''. Phosphate is a little low and water a little high, but closer agreement to theoretical values are shown in the analyses of rockbridgeite from Fletcher quarry.

Two samples of rockbridgeite from the Fletcher quarry, North

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[3] Frondel, Clifford, The dufrenite problem: *Am. Mineral.*, **34**, 528 (1949).

Groton, New Hampshire, were prepared, one of green unoxidized fibers and a second of brown oxidized fibers which correspond to $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ and $(Fe''', Mn'')Fe_4'''(PO_4)_3(OH)_5$. The Fe''/Mn'' ratio for the unoxidized sample is 1.46 (3/2). During oxidation the following changes occur: (1) oxidation of all the FeO to Fe_2O_3 and a minor amount of MnO to Mn_2O_3, (2) a relative increase in MnO, (3) a decrease in total iron and in phosphate, and (4) a decrease in water content. In the oxidized portion the excess of R_2O_3 over that required by the formula above is calculated to RO in order to obtain the ratios tabulated. The cell volume for rockbridgeite was not determined precisely by Weissenberg photographs, but approximately by powder photographs; the weight of the unit cell is 2531 for unoxidized material and 2535 for oxidized material. Ratios so derived are given in Table 3.

Frondelite is easily fusible to a magnetic globule. It is soluble in dilute HCl, but insoluble in HNO_3 and H_2SO_4; the Na_2CO_3 fusion is insoluble in HNO_3 but soluble in HCl; the $KHSO_4$ fusion is soluble in H_2SO_4. It yields water when heated in a closed tube.

The specific gravities were determined by the use of an Adams-Johnston pycnometer of fused silica. The slightly higher specific gravities than those reported by Frondel on rockbridgeite from the Fletcher quarry may possibly be due to removal of lighter fractions with methylene iodide in the course of purification of the author's samples. The specific gravities reported are representative of the sample analyzed.

The analyses of the minerals composing the rockbridgeite-frondelite series, as represented by analyses from Rockbridge County, Virginia, Fletcher quarry, New Hampshire, and the Sapucaia pegmatite, Brazil, establish the unoxidized series represented by $R''Fe_4'''(PO_4)_3(OH)_5$, with $R''=Fe$ for rockbridgeite from Rockbridge County, $R''=Fe/Mn=3/2$ for rockbridgeite from Fletcher quarry, and $R''=Mn$ for frondelite. Analyses of material from the Palermo pegmatite,[4] New Hampshire; from Polk County, Arkansas; and from the Fletcher quarry, New Hampshire, establish an oxidation sequence in which partial or complete oxidation of ferrous iron to ferric iron is followed by a minor amount of oxidation of MnO to Mn_2O_3. This follows the generally accepted plan of oxidation of all iron-manganese phosphate minerals, as described by Brian Mason,[5] in which iron oxidizes first, and may or may not be followed by oxidation of manganous manganese.

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[4] As used in this paper the term Palermo pegmatite serves only as a convenient means of reference and is not to be considered a stratigraphic name.

[5] Minerals of the Varutrask pegmatite. XXIII Some iron-manganese phosphate minerals and their alteration products, with special reference to material from Varutrask. Brian Mason. *Geol. Fören. Förhandl.*, **63,** 165–168 (1941).

X-RAY DATA

Single crystal rotation and Weissenberg pictures were taken about a cleavage fragment of frondelite so oriented that (1), (100) and (010) were in a zone parallel to the rotation axis $(=c)$; (2), (100) and (001) were in a zone parallel to the rotation axis $(=b)$; and (3), (010) and (101) were in a zone parallel to the rotation axis $=[10\bar{1}]$. All three orientations showed C_{2l} symmetry on the zero layer of the Weissenberg photographs; the first layer pictures were not equally well developed about both axes; hence it was not possible to differentiate between C_{2l} and C_l symmetry. An orthorhombic mineral is indicated. An extremely small cleavage fragment was chosen to minimize the effect of the radiating fiber structure; however the zero and first layers of the Weissenberg picture rotated around the fiber axis $=c$ showed the spots representing a single plane spread out as a thin line through a distance of several degrees. The Weissenberg pictures around other axes showed this effect far less, but the various levels of the rotation pictures around these axes were represented by small arcs rather than discrete points. The d values, however, could be measured accurately from the Weissenberg pictures; $a=13.89$, $b=17.01$, and $c=5.21$ Å. The volume of the unit cell is 1231 (Å)^3.

An examination of the projections on (hkl) showed $h+l$ even, k even or odd; on $(0kl)$ l even, k even or odd; on $(h0l)$ $h+l$ even, h odd if l odd; on $(hk0)$ h even, k even or odd, on $(h00)$ h even, on $(0k0)$ k even and on $(00l)$ l even; therefore the tentative space group is $B22_1$ or $B22_12$ (D_2^5). This space group requires a minimum of four molecules per cell.

The single crystal x-ray photographs were taken with copper radiation, nickel filter, on a very small irregular cleavage fragment, and it is possible that some of the extinctions observed may have been due to absorption, thus indicating a higher symmetry. The possibility of absorption is verified by unequal development of spots around the two axes on the first layer pictures, making it impossible to differentiate between C_{2l} and C_l symmetry. The powder photograph taken with iron radiation was therefore indexed to see whether all lines could be accounted for by indices consistent with the chosen space group. Since more than one solution to the equation

$$d^2_{hkl} = \frac{1}{\dfrac{h^2}{a^2}+\dfrac{k^2}{b^2}+\dfrac{l^2}{c^2}}$$

is possible, an exhaustive list of possibilities is not given, nor is the possibility of alternate indices not fitting the space group considered. The approximate cell dimensions of various members of the rockbridgeite-

Table 4. Possible Indices for Reflections Occurring on Powder Photograph of Frondelite

Iron Radiation, Manganese Filter

d observed	Indices for reflections also observed on Weissenberg photographs				Additional possible indices			
	Index	Theory	Index	Theory	Index	Theory	Index	Theory
8.59Å	020	8.51						
6.90	200	6.94						
6.46					210	6.431		
4.86	101	4.88						
4.69	111	4.69						
4.36					230	4.393		
4.23	040	4.25						
3.61	240	3.626						
3.441	400	3.473	301	3.461				
3.381	311	3.391	410	3.403				
3.195	321	3.205	420	3.214				
3.045	250	3.054						
2.949	430	2.960			331	2.954		
2.825	060	2.835						
2.779	151	2.791						
2.679	440	2.690			341	2.685		
2.597	002	2.605						
2.444	501	2.451	202	2.439[a]				
2.415	351	2.421	212	2.414				
2.340					222	2.345		
2.292	270	2.294			610	2.294		
2.234					232	2.224		
2.175	171	2.175						
2.121	080	2.126			242	2.115		
2.064	412	2.069			052	2.068		
2.030					422	2.024		
1.979	252	1.983						
1.957	181	1.949			432	1.956		
1.913					062	1.918		
1.849	701	1.852	262	1.849				
1.723					272	1.722		
1.694					123	1.689		
1.659	490	1.661			2.10.0	1.653		
1.598	1.10.0	1.606	323	1.597	143	1.597		
1.562					333	1.563		
1.537					153	1.537		
1.492	292	1.494						
1.472	353	1.468			1.11.1	1.474	163	1.473
1.411	4.11.0	1.413			3.11.1	1.412	363	1.410[b]
1.394					2.10.2	1.395		
1.360	1.12.1	1.361						
1.312	4.12.0	1.312			3.12.1	1.312		
1.259	1.13.1	1.263						
1.252					234	1.249		
1.223	4.13.0	1.224			10.02	1.226	2.12.2	1.226[c]
1.214					0.14.0	1.215	414	1.216[d]
1.189					434	1.192		
1.148					3.14.1	1.146	1.11.3	1.151

Additional indices:

[a] 161, 2.452, 450, 2.432.

[b] 492, 1.414.

[c] 244, 1.226.

[d] 1.10.3, 1.211.

TABLE 5. X-RAY POWDER SPACING DATA FOR THE ROCKBRIDGEITE-FRONDELITE SERIES
IRON RADIATION, MANGANESE FILTER

Rockbridgeite (6.14 FeO, 0.40 MnO) Rockbridge, County, Va.		Rockbridgeite (5.51 FeO, 3.73 MnO) Fletcher quarry, N. H.		Frondelite (MnO 4.10, no FeO) Fletcher quarry, N. H.		Frondelite (MnO 7.74, no FeO) Sapucaia pegmatite	
Intensity	*d*-Å	Intensity	*d*-Å	Intensity	*d*-Å	Intensity	*d*-Å
1	8.36	1	8.56	1	8.52	1	8.59
2	6.94	2	6.87	1	6.85	2	6.90
1	6.46			1	6.43	1	6.46
1	4.85	1	4.83	1	4.80	1	4.86
1	4.67	1	4.67			2	4.69
1	4.34	1	4.34			1	4.36
1	4.20	1	4.22	1	4.22	1	4.23
4	3.58	4	3.59	4	3.60	4	3.61
2	3.431	2	3.435	2	3.426	2	3.441
5	3.391	5	3.367	5	3.357	5	3.381
10	3.186	10	3.192	10	3.181	10	3.195
3	3.017	3	3.035	3	3.033	3	3.045
1	2.934	1	2.938	1	2.931	1	2.949
		1	2.811			1	2.825
3	2.763	3	2.770	3	2.773	3	2.779
2	2.670	2	2.673	2	2.661	2	2.679
2	2.589	2	2.587	2	2.597	2	2.597
		3	2.434	3	2.439	3	2.444
4	2.415	4	2.413	4	2.402	2	2.415
				1	2.332	1	2.340
2	2.269	2	2.279	2	2.282	2	2.292
1	2.26	1	2.220	1	2.196	1	2.234
1	2.169	1B	2.171			1	2.175
2	2.106	2	2.109	1	2.112	2	2.121
		1	2.060	1	2.060	2	2.064
2	2.019	1	2.021	1	2.02	2	2.030
3	1.966	2	1.971	2	1.976	3	1.979
						2	1.957
1	1.930			1	1.942	1	1.939
		1	1.914				
1	1.897	1	1.908			1	1.913
3	1.836	3	1.841	3	1.842	3	1.849
1	1.731					1	1.756
1	1.709	2	1.718	2	1.717	2	1.723
2	1.688	2	1.689	2	1.691	2	1.694
2	1.637	2	1.650	2	1.654	2	1.659
5	1.592	5	1.596	5	1.594	5	1.598
		1	1.570				
2	1.551	1	1.558	2	1.558	2	1.562
		2	1.535	2	1.534	2	1.537
1	1.513	1	1.517				
1	1.478	1	1.485	1	1.487	1	1.492
1	1.455	1	1.471	1	1.471	1	1.472
		1	1.406	1	1.406	1	1.411
1	1.393	1	1.393	1	1.388	1	1.394
						1	1.360
				1	1.305	1	1.312
2	1.255	1	1.256	1	1.255	1	1.259
1	1.244	1	1.249	1	1.249	1	1.252
		1	1.219	1	1.225	1	1.223
				1	1.206	1	1.214
		1	1.187			1	1.819
		1	1.148	1	1.144	1	1.148

frondelite series may be obtained from the powder photograph. These are: $a = 13.73$, $b = 16.82$, and $c = 5.18$ Å for rockbridgeite from Rockbridge County, Va., $a = 13.76$, $b = 16.94$, and $c = 5.19$ Å for rockbridgeite from Fletcher quarry, N. H., and $a = 13.72$, $b = 16.94$, and $c = 5.19$ Å for the oxidized rockbridgeite at Fletcher quarry.

In Table 5 are listed the x-ray powder spacing data for frondelite and data for members of the frondelite-rockbridgeite series. The material from the Sapucaia pegmatite represents the manganous end member. Rockbridgeite from Rockbridge County, Virginia, represents the ferrous iron end member; the unoxidized material from Fletcher quarry, New Hampshire, has a Fe''/Mn'' ratio of 3/2. The difference in cell size between the various members of the series is not easily observed by inspection of powder pictures, but careful measurements show a slightly smaller cell for the ferrous iron member than for the manganous end member.

SUMMARY

Frondelite, $Mn''Fe_4'''(PO_4)_3(OH)_5$, occurs as brown radiating fibers at the Sapucaia pegmatite, Brazil. It is isomorphous with rockbridgeite $Fe''Fe_4'''(PO_4)_3(OH)_5$ from Rockbridge County, Virginia. An intermediate member of the series $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ with $Fe''/Mn'' = 3/2$ occurs at Fletcher quarry, New Hampshire; the latter oxidizes to $(Fe''', Mn'')Fe_4'''(PO_4)(OH)_5$.

ACKNOWLEDGMENTS

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VARIATIONS IN DIFFERENTIAL THERMAL ANALYSIS CURVES OF SIDERITE*

Richards A. Rowland and Edward C. Jonas

Abstract

The several reported variations in DTA curves of siderite are reproduced from samples of the same siderite by varying the particle size, dilution, and tightness of packing. The relationship between these variables and the suppression of the endothermic loop associated with the loss of CO_2 is shown by a set of curves. By controlling the ambient furnace atmosphere, with a cover over the sample or with an inert gas, the exothermic loops accompanying the oxidation of the iron oxide resulting from decomposition of the $FeCO_3$ can be delayed or completely suppressed. The results of *x*-ray diffraction studies of samples heated to several different temperatures are used in interpreting the DTA curves.

The method of differential thermal analyses is based on the simultaneous heating in a furnace of two substances, one, the material to be analyzed, the other, an inert substance which is known to undergo no phase changes nor chemical reactions in the temperature range to be studied. As the temperature of the furnace is raised at a regular rate, the difference in temperature between the two substances is measured and recorded. By convention, exothermic deflections, when the sample temperature is greater than the temperature of the inert material, are oriented upwards, and endothermic deflections are oriented downward.

With the recent improvement of DTA techniques and their application to the study of fine-grained sediments, there has developed the problem of detecting and identifying non-argillaceous minerals that may be present in sediments. Differential thermal analysis curves for various clays are reasonably well defined, and the relatively pure minerals can usually be recognized. However, while the presence of some accessory minerals has but little effect on the characteristic clay curve, others, even in small quantity, interfere with the diagnostic portion of the curve. One such mineral, which is frequently associated with petroleum-bearing sediments, is siderite, and with it perhaps the entire iron-manganese carbonate series.

The differential thermal analysis of siderite has been the subject of considerable comment since the publication by Cuthbert and Rowland (*Am. Mineral.*, 1947, p. 114) of a siderite curve with a single exothermic peak at about 560° C. They attributed this peak to "the heat balance between the decomposition of $FeCO_3$ and the immediate oxidation of the resulting FeO to Fe_2O_3." This curve was part of a preliminary study of some carbonate minerals, each of which was diluted 1:3 with γ-Al_2O_3.

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The experimental work was completed in 1941 but delayed in publication by the authors' preoccupation with National Defense. That other workers were obtaining siderite curves consisting of an endothermic peak followed by an exothermic peak was recognized by the authors in a letter to the editor (*Am. Mineral.*, 1947, p. 591). Shortly thereafter Kerr and Kulp (*Am. Mineral.*, 1947, p. 679) published curves of siderite from a dozen different localities. Each of these curves had an endothermic peak between 520° and 650° C. followed after an interval by a variety of exothermic peaks. They raised the question as to how immediate is the oxidation of FeO to Fe_2O_3 after the loss of CO_2. Frederickson (*Am. Mineral.*, 1948, p. 373) confirmed the immediate oxidation of the FeO after the loss of CO_2 but was unable to duplicate the curve of Cuthbert and Rowland.

The effect of heating on siderite involves conditions not generally encountered in the thermal analysis of most minerals. When decomposition takes place and CO_2 is liberated from the $FeCO_3$, the remaining FeO is very susceptible to oxidation. Whether the oxidation occurs simultaneously with, immediately after, or somewhat later than the loss of CO_2 may be dependent on the rate at which the CO_2 can escape and allow air to enter.

Assuming that the reactions are:

$$FeCO_3 \rightarrow FeO + CO_2$$
$$4FeO + O_2 \rightarrow Fe_2O_3,$$

the volume of oxygen gas required to complete the oxidation stage is about one fourth of the volume of CO_2 given off in the decomposition stage. In terms of air volume required to supply the necessary oxygen, for ideal gas behavior, this amounts to approximately 325 cc. of air at 500° C. for 0.5 gram sample. If the final product is $FeO \cdot Fe_2O_3$, then approximately 235 cc. of air at 500° C. would be required. The effect of varying the tightness of packing, particle size, and dilution on the diffusion of these gases through the sample, as reflected in the character of the differential thermal analysis curve, has been partially investigated here.

The differential thermal analysis apparatus with which this study was made is similar to that described by Grim and Rowland (*Am. Cer. Soc.*, 1944, p. 65) except that the furnace temperature is measured by a recording potentiometer, and the deflections of the temperature-difference galvanometers are visibly recorded by Beckman Photopen Recorders. The sample well holds approximately 0.5 gram, and is 0.25 inch in diameter and 0.375 inch deep. The heating program for each sample was 10° C. per minute from room temperature upward. A specimen of Roxbury, Connecticut, siderite, supplied by Ward's Natural Science Establishment, was ground to pass the 60-mesh screen and used as the supply from which each of the samples used in the following experiments was taken. Each of the curves considered was duplicated several times and the following figures represent more than 100 differential thermal analyses.

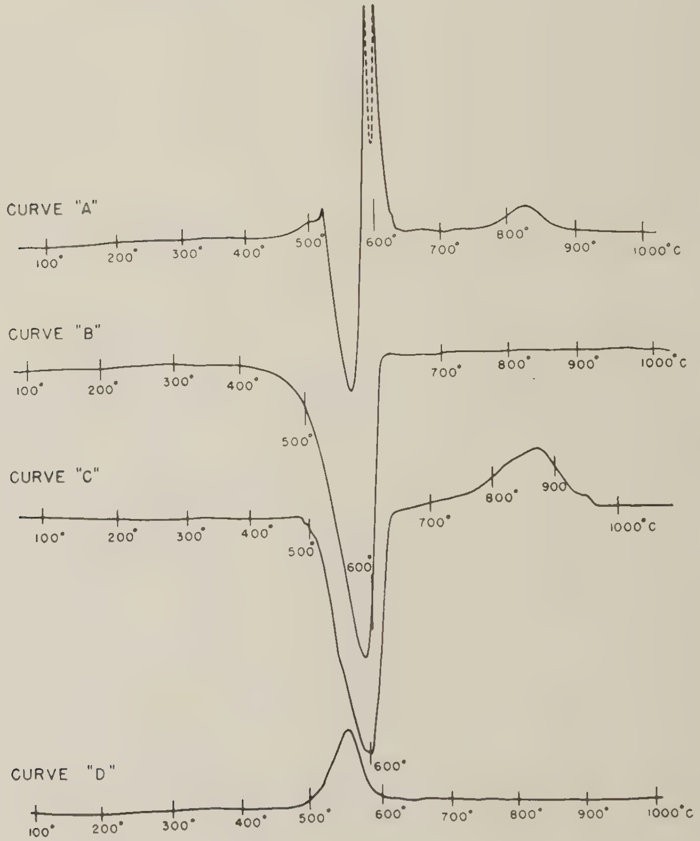

FIG. 1

Figure 1 shows the curves obtained when samples of this siderite were heated under different conditions. Curve "A" was obtained by firmly packing the ground siderite into the sample well and omitting the cover on the sample holder so that the top of the specimen was exposed to the furnace atmosphere. The endothermic peak accompanying the loss of CO_2 is interrupted by an exothermic peak presumably arising from the oxidation of FeO. Curve "B" was produced when a similarly packed sample was heated in a furnace atmosphere of nitrogen; here the exothermic peaks are suppressed. A similar curve is obtained in a CO_2 atmosphere. Curve "C" was obtained with a cover over the top of a sample otherwise prepared and heated as in curve "A." The broad exothermic peak, which occurs after the endothermic peak associated with the loss of CO_2 is completed, varies in shape and temperature of occurrence even when representing the same sample. The curve is similar to those published by Kerr and Kulp. Curve "D" was obtained when very finely ground siderite was loosely packed in an uncovered sample well. The curve, with its single exothermic peak, is like the curve published by Cuthbert and Rowland, and is also similar to the curve "H" in Fig. 2, obtained by diluting siderite with alundum.

An *x*-ray diffraction study was made of the products obtained when the heating was stopped at 700° C. At 700° C. each sample contains hematite and a spinel, the diffraction pattern of which resembles magnetite. Samples heated and cooled to room temperature in an atmosphere of nitrogen (curve "B") have only spinel lines and the $d=4.27$ Å line of magnetite is strong. Samples heated with a cover, curve "C," contain more than 90 per cent of this spinel. Samples heated without a cover, curve "A," contain about 60 per cent spinel and 40 per cent hematite. The product obtained from loosely packing fine-grained siderite, curve "D," contains about 30 per cent spinel and 70 per cent hematite. Chemical analysis of a sample heated without a cover, curve "A," shows less than 0.4 per cent ferrous iron; *x*-ray diffraction studies of the products at 1000° C. show essentially the same constituents but an increased amount of hematite. In each case, the material is magnetic.

In order to learn whether the exothermic dome between 750° C. and 850° C., curve "A," is associated with an oxidation, a sample was heated in a nitrogen atmosphere, like curve "B," to 1000° C. and cooled in the same atmosphere to 300° C. When the nitrogen was replaced with air an exothermic deflection commenced immediately. When this exothermic deflection was complete the sample was again heated to 1000° C. in an atmosphere of nitrogen. The curve obtained had an exothermic dome between 750° and 850° C. The absence of this dome in a nitrogen atmosphere after the loss of CO_2, and its presence even when material which has been exposed to the air is heated through this range in an atmosphere of nitrogen, suggests that the dome is not associated with an oxidation but probably indicates a change in one of the products of the previous oxidation. The nature of this change is unknown but it may be that the material at 700° C. contains an appreciable amount of γ-Fe_2O_3 which is not readily identifiable when mixed with magnetite, and which may change over to hematite between 750° and 850° C. This may also account for the increase in hematite observed between 700° and 1000° C.

The corresponding dome on curve "C" is very much larger and is located on a gently sloping exothermic deflection. The absence of a sharp exothermic peak following the endothermic peak is due to a cover over the sample. This cover prevents the rapid escape of CO_2 and does not allow air to enter readily. Of six curves prepared in the same fashion, not one duplicated the shape or position of the exothermic dome. Apparently it is impossible to adjust the cover so that its effect on the passage of gas is reproducible. Furthermore, the endothermic peak is not fully representative of the heat absorbed by the loss of CO_2 because the air trapped in the sample is enough to oxidize some of the FeO. The oxidation seems to take place just after the decomposition of $FeCO_3$ begins and is thought to account for the difference between curves "B" and "C" between 400° C. and 500° C. Curve "B" undergoes no oxidation in this range while curve "C" represents the net heat effect resulting from the loss of CO_2 and the immediate oxidation of the resulting FeO. Curve "A" represents a sample having free access to the air at the outset; consequently, this net effect is more pronounced. Curve "D" not only had free access to the air but also an adjusted rate of evolution of CO_2 and demand for air. Consequently as each grain of siderite decomposes, the CO_2 can escape and the FeO can be oxidized. The curve then represents a heat balance between the decomposition of $FeCO_3$ and the immediate oxidation of the resulting FeO. The curves obtained in passing from a curve like "A" to one like "D" are illustrated in Fig. 2.

The curves in Fig. 2 were produced from sized siderite at several different dilutions with sized alundum. The siderite was ground to pass the 240-mesh screen and to remain on the 270. The alundum passed the 80-mesh screen and remained on the 100. Each sample was packed into the sample holder so that the effect of packing would be as nearly identical as possible. It can be seen that as the amount of siderite decreased, the endothermic peak associated with the loss of CO_2 decreased more rapidly than did the following exothermic peak until in curve "H" the endothermic peak is suppressed. It is thought that this progressive suppression of the endothermic effect is due to the increased ease with which the CO_2 can escape and allow the FeO to come into contact with the air. Some of the factors which may control this are: the permeability of the packed sample, dependent on both the tightness of packing and the sorting of grain size; and the amount of CO_2 evolved at a given point, dependent on the dilution of the siderite, its grain size and its distribution over the surface of the diluent. A tight packing or an unassorted distribution of siderite makes passage of gas more difficult. A diluted sample reduces the quantity of CO_2 and leaves a proportionate larger amount of air in contact with the grains. Increased surface area permits decomposition and unhindered loss of CO_2 as soon as each grain reaches the proper temperature and thereby allows the reaction to become complete as soon as possible. No steady stream of CO_2 then prevents the access of air to the FeO.

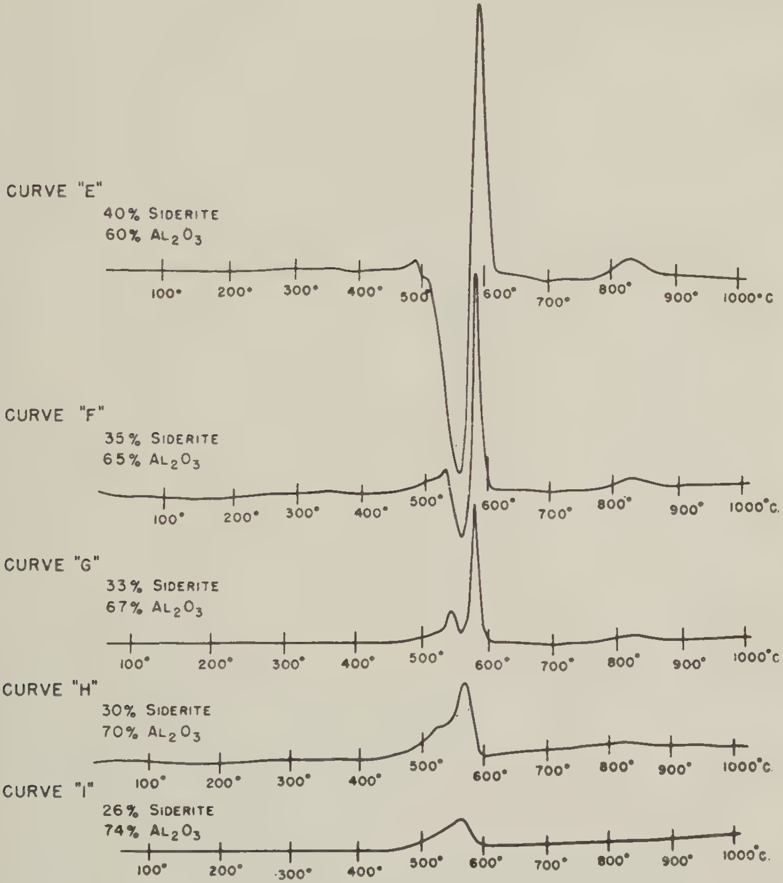

Fig. 2

Higher permeability and easier access for incoming air exists between the wall of the sample well in almost any granular packing. Therefore, it is to be expected that some of the FeO will be oxidized immediately after the loss of CO_2. Furthermore, some air is trapped in the sample even when a cover is used. The exothermic deflection near 500° C. on curve "C," by contrast with curve "B," is thought to result from this effect.

Several sets of differential thermal curves, similar to those presented in Fig. 2, were obtained for mixtures of different sizes of siderite and alundum. In each set of differential thermal curves for a given siderite-alundum size ratio when the siderite content was reduced to a certain percentage, the endothermic loop between 500° C. and 600° C. did not go below the zero line (like curve "G"). Figure 3 presents a summary of these differential thermal curves. It should be emphasized that the numerical values associated with these curves are a characteristic of the apparatus employed. Similar curves, with perhaps different numerical values, should be obtainable with any apparatus not employing a cover over the specimen-well. In Fig. 3 the percentage of siderite is plotted as the ordinate, the sieve size of the alundum as the abscissa, while the points on each curve indicate the sieve size of the siderite. These curves present the effect of two conditions of heterogeneous packing with low porosity and permeability and two conditions of open packing of nearly

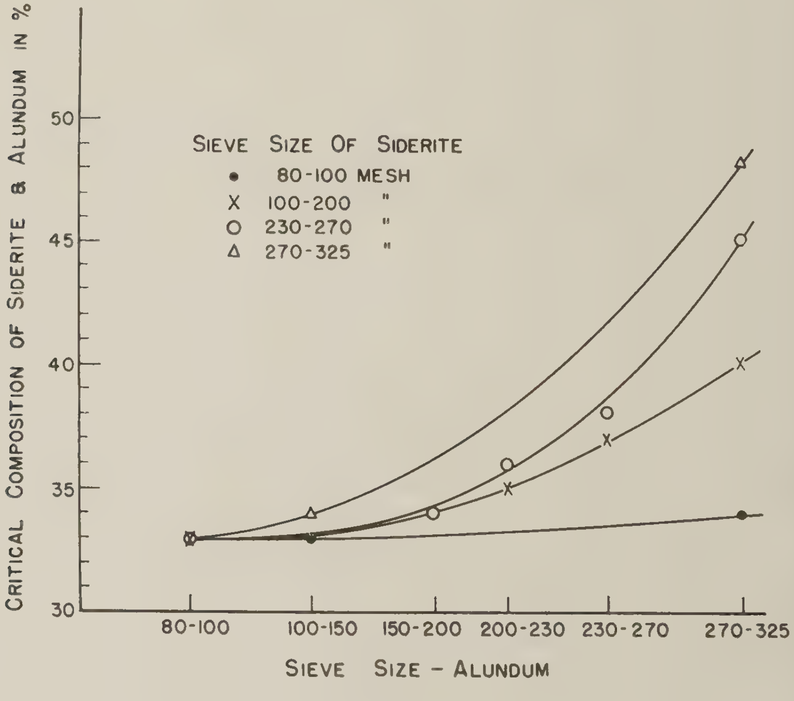

Fig. 3

equidimensional grains. When the grain size of either constituent is large with respect to the other, the percentage of siderite at which the endothermic loop is suppressed is about the same (33 per cent). In the open packing when the grains of both siderite and alundum are small, the suppression begins at a higher percentage of siderite. When both siderite and alundum are coarse the suppression is obtained only when the siderite is reduced to a percentage about that of the heterogeneous mixture. Even with an open packing, larger grains of siderite increase the total time during which the evolution of CO_2 occurs, and this apparently slows up the entry of air enough to prevent the immediate oxidation of the FeO. Since three of the four conditions give similar results perhaps greater reproducibility can be obtained from artificial mixtures so prepared. When siderite is found disseminated through a sediment, a heterogeneous distribution is most likely. If the siderite constitutes less than 25 per cent of the sediment, the differential thermal analysis curve probably will be a single exothermic loop.

From this study of siderite one aspect of the method of differential thermal analysis has been partially clarified. The variety of thermal analysis curves which are obtained for siderite under various controlled conditions such as: with the top of the specimen well open to the air, covered, and in an inert gas, clearly indicates the effect of the ambient furnace atmosphere. Its accessibility to the sample is varied by controlling the grain size, dilution, and tightness of packing of the sample.

Thermal analysis curves for minerals which decompose rapidly are not reproducible when made with the sample-well covered because the pressure and rate of diffusion are not controlled. When the evolved gas is allowed to escape freely, this complication is eliminated. If the product remaining after the gas is evolved is susceptible to oxidation, air either must be excluded completely by an inert furnace atmosphere, or allowed to enter freely. When the product is allowed to oxidize, the resulting temperature-difference curve represents the net effect of the heat balance between decomposition and oxidation if the two reactions take place in the same temperature range.

A furnace atmosphere of inert gas suppresses the oxidation reaction. The resulting curve indicates the temperature at which the decomposition begins and represents only the heat involved in the decomposition. The oxidation reaction can be accelerated to such an extent by using finer grain size, by diluting the sample with inert solids, or by packing the sample more loosely, that the decomposition is entirely masked by the oxidation reaction and a curve with only an exothermic deflection results. Because siderite disseminated in petroleum-bearing sediments is both fine-grained and dilute, the exothermic deflection by itself is the most frequently encountered indication of the presence of siderite in such sediments.

Certain other minerals such as rhodochrosite, cerussite, and some of the basic carbonates, whose thermal decomposition is followed by an oxidation, would be expected to give similarly variable thermal analysis curves.

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MUSCOVITE WITH SMALL OPTIC AXIAL ANGLE*

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Contents

Abstract 559
Introduction 559
Occurrence 559
Related Studies 560
Description and Optical properties 561
Chemical composition 564
Thermal analysis 565
X-ray studies 565
  Powder pattern 565
  Laue photographs 566
  Rotation and Weissenberg photographs 566
Summary 572
Acknowledgments 572

Abstract

Muscovite with unusual optical and structural characteristics is described. The size of the optic axial angle (2V) varies from about 15° for areas of highest birefringence in the cleavage plane to about 3° for areas of lowest birefringence. *X*-ray studies show the muscovite to be three layered monoclinic with $Z=a$ and thus dimorphous with previously described muscovites. Variation in the observed optic axial angle is attributed to the coalescence of the optical effects of superposed twin elements.

Introduction

In the course of field investigations near the Sunrise Copper Prospect, Sultan Basin, Snohomish County, Washington, J. J. Collins collected a white mica that was later identified as a muscovite with very unusual optical and structural characteristics. C. S. Ross found it to be nearly uniaxial and suggested further study of the material.

Occurrence

A. C. Waters collected additional material and made a brief examination of the field relations. His description follows:

"A white, nearly uniaxial muscovite occurs as veinlets and replacements in the granodiorite near the Sunrise Copper Prospect, Sultan Basin, Snohomish County, Washington. The mica occurs as both fissure and 'replacement veins' ¼ to 1 inch thick which commonly appear along closely spaced partings or sheeting in the granodiorite. In part the mica appears to have been formed by selective replacement of the granodiorite, for, although at some localities the position of the feldspars is occupied by mica, the original quartz grains are intact. Hot gases, following the sheeting in the granite rock, probably were the agents that formed the mica. The process probably is similar to greisenization.

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"The mode of occurrence of the mica bears a striking resemblance to the occurrence of siderophyllite in 'replacement veins' in the Tertiary granite of the Mourne mountains in Northern Ireland, described by Nockolds and Richey.[1] The field relations and general appearance of the veinlets at the Sunrise Prospect are similar to those in the Mournes."

RELATED STUDIES

Muscovites with small optic axial angles have been reported in the literature, but they are rare. Carl Schmidt[2] found, in a gneiss from the Adula Mountains, Switzerland, a green pleochroic muscovite that was uniaxial. It became biaxial on heating and on cooling became uniaxial again. Kunitz[3] reported a uniaxial muscovite in mica schist from Mt. Mucrone. After the ignition of the mica flakes Kunitz could detect no substantial change in the size of the optic axial angle. Recently Postel and Adelhelm[4] described a white muscovite in the Wissahickon formation with low values of 2V varying between 22° and 50°. Laue photographs of the mica showed radial diffuseness or "asterism," and Postel and Adelhelm suggested that the degree of radial diffuseness might be connected with the low and varying values of 2V observed on the mica.

A detailed analysis of the structure of muscovite was made by Jackson and West.[5] Hendricks[6] has shown that the structure of other micas is more complex, and that most of them are polymorphic, the polymorphism resulting from different arrangements of the layers. Hendricks found no polymorphism in muscovite; all 19 studied specimens had the same two-layer monoclinic structure. In every specimen the optic axial angle (2V) was between 34° and 50°, and the plane of the optic axes was normal to the *b* axis. He found that the distinguishing feature of the muscovite structure is a distortion from the ideal structure shown by the presence of certain reflections absent for the ideal structure. This distortion results from the incomplete filling of the octahedral positions and was considered by Hendricks to be the factor leading to a unique requirement on the successive stacking of layers.

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[1] Nockolds, S. R., and Richey, J. E., Replacement veins in the Mourne Mountains granites: *Am. Jour. Sci.*, **237**, 27–47 (1939).

[2] Schmidt, C., Die Gesteine des Adulamassivs: *Beitr. Geol. Karte Schweiz, Anhang Lief.*, **25**, 32 (1891).

[3] Kunitz, W., Die Beziehungen zwischen der chemischen Zusammensetzung und den physikalisch-optischen Eigenschaften innerhalb der Glimmergruppe: *Neues Jahrb., Beilage-Band*, **50**, 383 (1924).

[4] Postel, A. W., and Adelhelm, W., White mica in the Wissahickon complex: *Am. Mineral.*, **29**, 279–290 (1944).

[5] Jackson, W. W., and West, J., The crystal structure of muscovite: *Zeit. Kryst. Min.*, **76**, 211–227 (1930).

Jackson, W. W., and West, J., The crystal structure of muscovite: *Zeit. Kryst. Min.*, **85**, 160–164 (1933).

[6] Hendricks, S. B., and Jefferson, M. E., Polymorphism of the micas: *Am. Mineral.*, **24**, 729–771 (1939).

For many of the micas Hendricks found appreciable diffuse scattering in Weissenberg photographs along $(h_a k_a l)$, $k \neq 3n$ curves. This showed up as radial streaks in Laue photographs of the micas taken with the incident x-ray beam normal to the cleavage plane. Both were explained in terms of constant h and k indices with continuous variation of the l index resulting from a variable periodicity in the stacking of the mica layers in such a manner that planes with the k index a multiple of three were apparently undisturbed. He did not find diffuse scattering for any muscovite.

Asterism was encountered by Postel and Adelhelm in Laue patterns of muscovite and the Sultan Basin muscovite exhibits similar radial diffuseness. H. C. Vacher[7] observed that permanent asterism could be developed or increased in micas by heating biotite or phlogopite to about 500° C. or muscovite to 800° C. The asterism developed in phlogopite at 190° to 385° mostly disappeared on cooling.

Description and Optical Properties

The mica from Sultan Basin consists of wedge-shaped aggregates of trowel-shaped crystal segments. The segments, about $4 \times 3 \times \frac{1}{2}$ millimeters in size, are ruled parallel to the directions AC and AD of Fig. 1(a), and much of the surface is ribbed or corrugated parallel to these rulings. There is a slight bending along AB (variable from crystal to crystal) so that the mica flakes do not lie completely flat on a slide. The segments cleave into thin elastic laminae that often split along the rulings to form narrow strips. These rulings, by analogy with muscovite in general, correspond to traces of glide planes or to pressure lines.

Under crossed nicols the flakes are seen to be twinned and AB in Fig. 1(a) may be taken as the trace of the composition plane. AB appears only under crossed nicols and as a narrow region of low birefringence. It is presumably the result of intergrowth or superposition of twins in the area as this region is almost uniaxial ($2V = 3°$). The twinning is repeated in a few crystals so that if extended further it would give forms with pseudohexagonal symmetry. The direction of the optic axial plane in each half of the flake and in the region AB is shown in Fig. 1(a). In the twins it is parallel to RS and RT and the direction is invariant over the whole of each twin. The relative orientation of the rulings and the axial plane indicate that $Z = a$ and the mica is in the second class of Reusch[8] used by

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[7] Vacher, H. C., in Hidnert, P., and Dickson, G., Some physical properties of mica: *Jour. Research, Nat. Bur. Standards,* **35**, 339–342 (1945).

[8] Reusch, E., Über die Kornerprobe am zweiachsigen Glimmer: *K. Akad. Wiss., Berlin, Monatsberichte,* 429 **(1868)**.

Dana.[9] The twinning axis for the common mica twin law is [310] which, for $Z=a$, is normal to AB, and in the cleavage plane. A rotation of 180° about the twin axis gives an apparent rotation of the axial plane in the cleavage plane of 60°. Part I is therefore related to Part II by the common mica twin law; the composition surface is normal to the twinning axis.

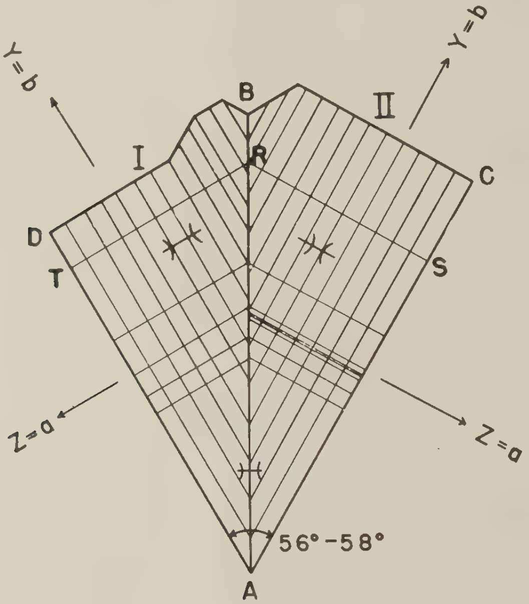

FIG. 1(*a*). Optical orientation.

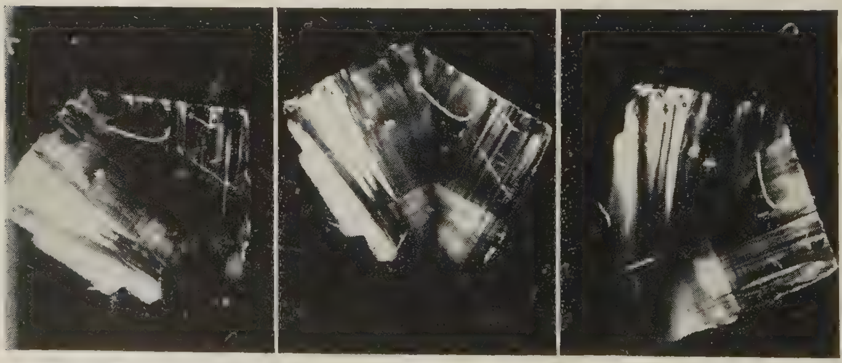

FIG. 1(*b*). Photomicrographs with crossed nicols.

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[9] Dana, E. S., and Ford, W. E., A Textbook of Mineralogy, 4th ed., p. 658 (1932).

Striations parallel to *RS* and *RT* appear under both uncrossed and crossed nicols. They are faint under uncrossed nicols and may be due to the slight differences in index of refraction. Under crossed nicols these striations, for the most part, are sharp and appear as bands of lower and higher birefringence. Striations parallel to *AC* and *AD* are due to bends and cracks in the crystal. No spot could be found on a dark streak parallel to *AC* or *AD* which did not at some point in the rotation of the flake between crossed nicols become as bright as the rest of the band parallel to *RS* or *RT* in which it lay. The size of the optic axial angle (2V) for the bands of lower birefringence is always smaller than 15°, the value approached by the bright areas, and varies from area to area. The lower the birefringence the smaller 2V becomes; it is 3° for areas of lowest birefringence. In these regions the isogyres are also more diffuse.

Any explanation of the variation based on twinning such that the orientation of the cleavage plane would be changed is ruled out, because any such regions with the cleavage plane not perpendicular to the light path would show a higher instead of a lower birefringence. The low 2V may, however, be a result of superposition of twins such as occurs at *AB*. The net result is as if equal amounts of I and II were rotated clockwise 60° and made to interleave with I, or rotated counterclockwise 60° and made to interleave with II. The combination would consist of equal thicknesses of mica superimposed at all angle multiples of 60° and may be formed by repeated twinning according to the mica law with composition plane (001). It would be essentially the same as one of the combinations mechanically built by Reusch[10] which he describes as giving an almost perfect uniaxial figure. The varying size of 2V would then result from combinations of the rotated members with varying amounts of the unrotated twin I or II. The bands of lower and higher birefringence require additional composition planes approximately parallel to (010).

From another viewpoint, the mica has a different crystal structure in the regions showing a smaller optic angle. Only two structures need be involved to produce all the effects described, as varying amounts of the two structures combined in parallel orientation would give the various differences in the size of the optic axial angle. *X*-ray work described in a following section did not reveal any definite structural difference so that the first explanation is taken as the more probable one.

The optical properties of the muscovite from Sultan Basin were measured in white light on portions of flakes showing maximum birefringence in the cleavage plane.

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[10] Reusch, E., Untersuchung über Glimmercombinationen: *Poggendorff's Annalen*, **138**, 628–638 **(1869)**.

Biaxial negative: $\alpha = 1.555 \pm .003$ $2V = 15° \pm 3°$
$\beta = 1.589 \pm .003$ $Z = a$
$\gamma = 1.590 \pm .003$
Pleochroism feeble: X = pale yellow with some green,
Y = Z = deeper yellow with more green.

The α index was measured on several small cleavage plates of mica standing on edge in flour dough with their protruding ends immersed in index oil. The values of the indices are somewhat uncertain because of the corrugated nature of the material, but are sufficiently accurate to establish that the maximum birefringence is the same as in the more common muscovite. The values of β and γ agree closely with Winchell's[11] data on the muscovite system.

CHEMICAL COMPOSITION

The chemical analysis of the mica from Sultan Basin is given in Table 1. The calculation of the atomic ratios was made by the method devised by Stevens[12,13] on the basis of 22 anion and cation equivalents in the simple mica formula. The formula obtained is that of muscovite.

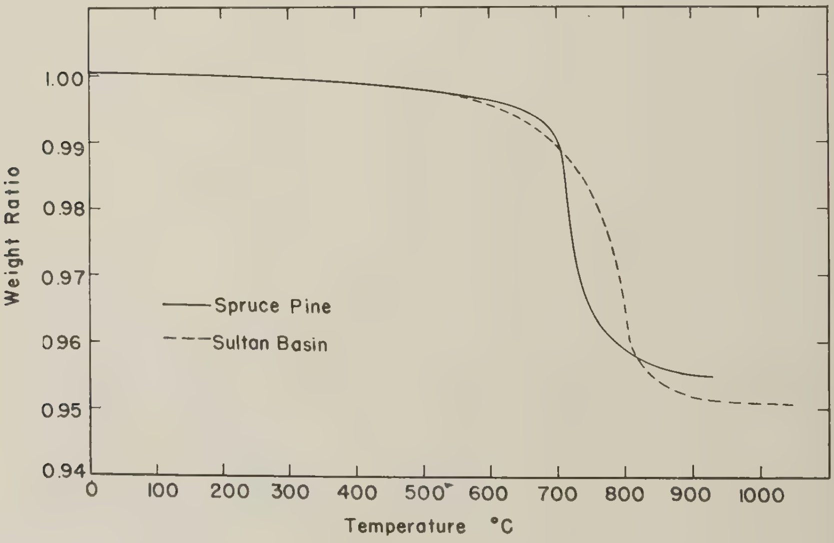

FIG. 2. Thermal dehydration curves.

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[11] Winchell, A. N., Elements of Optical Mineralogy, Part II, p. 268 (1933).

[12] Stevens, R. E., New analyses of lepidolites and their interpretation: *Am. Mineral.*, **23,** 607–628 (1938).

[13] Stevens, R. E., A system for calculating analyses of micas and related minerals to end members: *U. S. Geol. Survey, Bull.* **950,** 101–119 (1946).

TABLE 1. ANALYSIS OF THE MICA FROM SULTAN BASIN, SNOHOMISH COUNTY, WASHINGTON

		Equivalents		Atomic Ratios	
		e	$e'=3.993e$		
SiO_2	46.77	3.113	12.43	Si	3.11
				Al	.89
				Σ Tetrahedral	4.00
Al_2O_3	34.75	2.044	8.16	Al	1.83
Fe_2O_3	.71	.028	.11	Fe+++	.04
FeO	.77	.021	.08	Fe++	.04
MgO	.92	.046	.18	Mg	.09
TiO_2	.21	.011	.04	Ti	.01
				Σ Octahedral	2.01
CaO	.13	.005	.02	Ca	.01
Na_2O	.47	.015	.06	Na	.06
K_2O	10.61	.225	.90	K	.90
BaO	.13	.002	.01	Ba	.01
		5.509	21.99	Σ Large Cation	0.98
F	.16	.008	.03	F	.03
Total H_2O	4.48	.497	1.98	OH	1.98
	100.11			F+OH	2.01
Less O=F	.07	Formula:			
Total	100.04	$(KNaCaBa)_{0.98}(AlFe''Fe''' MgTi)_{2.01}$			
Specific Gravity	2.82	$(SiAl)_{4.00}O_{10.01}(F, OH)_{2.01}$			

Spectrographic examination by K. J. Murata showed, as the only other constituents: $Li_2O=0.02$, and $Rb_2O=0.05$.

THERMAL ANALYSIS

P. G. Nutting determined the thermal dehydration curves of the muscovite from Sultan Basin and of a muscovite from Spruce Pine (*Am. Mineral.*, **27,** 527, 1942; *Am. Mineral.*, **24,** 759, 1939). The latter represents a common muscovite. The results are plotted in Fig. 2. The muscovite from Sultan Basin gives off the last of its water at a slightly higher temperature (about 50°) than does the muscovite from Spruce Pine, but this is within the limits of variation for muscovite.

X-RAY STUDIES

Powder patterns

The powder pattern of the mica had only minor differences from the patterns of muscovites from eleven other localities. The patterns of the eleven other muscovites were identical, the pattern of the muscovite from Sultan Basin differing from them in that it had no lines at 2.99 Å, 3.20 Å, 3.49 Å, and 4.12 Å, and a stronger line at 3.10 Å. Fig. 3 illustrates the two patterns and the measurements are given in Table 2.

Laue Photographs

Laue photographs with the beam perpendicular to the cleavage plane were taken in an attempt to determine the symmetry of the muscovite from Sultan Basin and to detect structural differences between areas with large 2V and areas with small 2V. Over 20 specimens were carefully cut out from areas showing a minimum of warping. When mounted on a two-circle goniometer for orientation they gave poor signals indicating that they were warped. Unavoidable small variations from the nominal orientation caused more difference in the appearance of the Laue patterns in regard to intensities and positions of spots than any structural differences among the samples, and therefore no reliance was placed on Laue patterns for symmetry determination. All patterns were, however, approximately trigonal and all showed some asterism. Fig. 4 (*b*) illustrates a typical Laue pattern. Fig. 4 (*a*) and 4 (*c*) were taken using the same flake and illustrate effects produced when the *X*-ray beam is not perpendicular to the cleavage plate. The latter are shown to indicate some of the changes that warping could produce.

Rotation and Weissenberg Photographs

Rotation pictures about the normal to the cleavage plane had layer lines corresponding to a 30 Å spacing. Inasmuch as the thickness of a mica sheet is 10 Å, the muscovite from Sultan Basin has a unit cell three layers high. This is the first muscovite for which a unit cell other than two layers high has been found.

Weissenberg photographs were then used with some success to study the symmetry of the muscovite from Sultan Basin. An area with a small optic axial angle (2V=3°) was first chosen and because of the three-layered structure, we looked first for rhombohedral symmetry. Weissenberg photographs were taken rotating the crystal fragment about [010], [110], [310], [100], [3$\bar{1}$0], and [1$\bar{1}$0] on the basis of $Z=a$ and a monoclinic cell. If the crystal were trigonal the patterns for [110], [1$\bar{1}$0], and [100] should be identical as also the patterns for [310], [010], and [3$\bar{1}$0]. Examination of the patterns revealed that [110] and [1$\bar{1}$0] were identical while [100] differed slightly only with respect to diffuseness in the $(h_a k_a l)$ zone lines. The same differences held for the *b* axis and pseudo *b* axis pictures. Figure 5 illustrates Weissenberg photographs taken about [110], [1$\bar{1}$0], and [100]. An area with 2V=13°, whose Laue pattern is

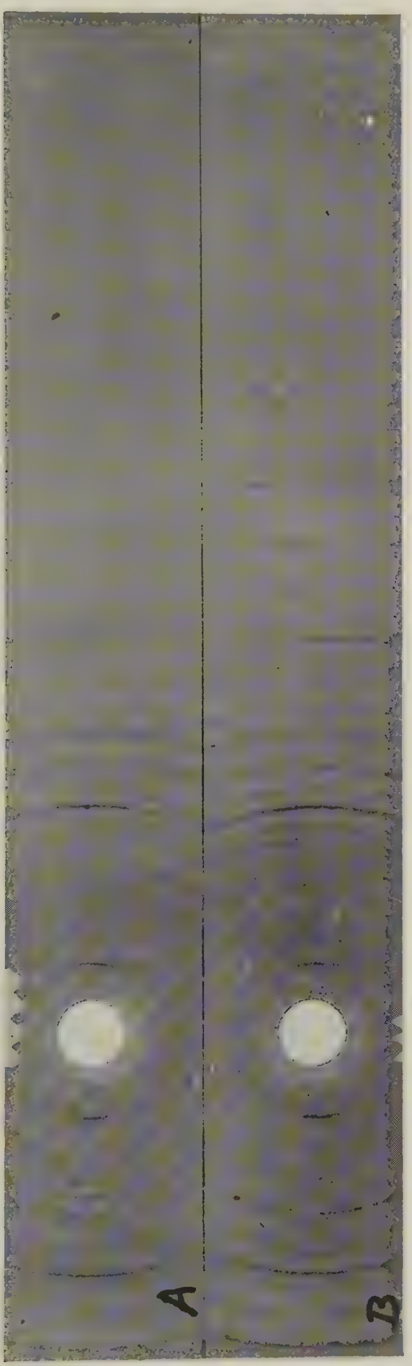


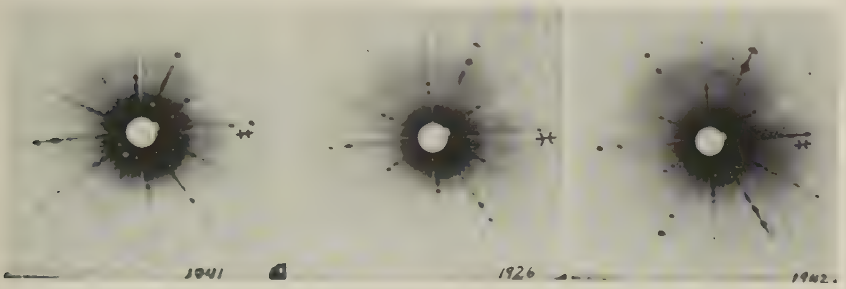
FIG. 3. X-ray powder photographs.
(A). Two layer muscovite from Keystone, S. D.
(B). Muscovite from Sultan Basin.

TABLE 2. *X*-RAY POWDER PATTERNS OF MUSCOVITE

Sultan Basin Fe radiation, unfiltered $\lambda = 1.938$Å		Common muscovites ASTM FILE, II 2177	
d	*I*	*d*	*I*
9.97	10	10.01	8
4.97	7	4.98	6
4.47	6	4.48	9
4.29	1	4.30	4
		4.12	4
		3.96	2
3.86	4	3.88	4
3.68	6*	3.72	5
3.59	2	3.56	2
		3.49	5
3.32	10	3.33	9
		3.20	6
3.10	4	3.1	2
		2.99	6
2.87	6	2.87	5
2.82	4	2.78	5
2.58	4	2.58	4
2.55	7	2.56	10
2.49	4	2.49	4
2.45	4	2.46	4
2.38	4	2.38	6
2.34	2	2.31	4
2.24	1	2.24	4
2.19	4	2.20	3
2.13	6	2.13	6
2.05	1	2.05	2
1.997	8	1.99	8
1.960	4	1.95	4
1.819	2	1.82	2
1.723	4	1.76	4
1.650	6	1.65	7
1.606	2	1.60	4
1.516	4		
1.500	6		
1.426	2		
1.347	6		
1.296	4		
1.248	6		
1.222	2		
1.053	4		

* At least partly β radiation from 3.32.

illustrated in Fig. 4 (*b*), was also checked in this manner with similar results. No significant differences between corresponding Weissenberg patterns of areas with small 2V and large 2V could be detected. The



(*a*) (*b*) (*c*)

Fig. 4. Laue photographs.
(*a*). Beam in the axial plane at 85° to the cleavage plane.
(*b*). Beam normal to the cleavage plane.
(*c*). Beam in the axial plane at 95° to the cleavage plane.

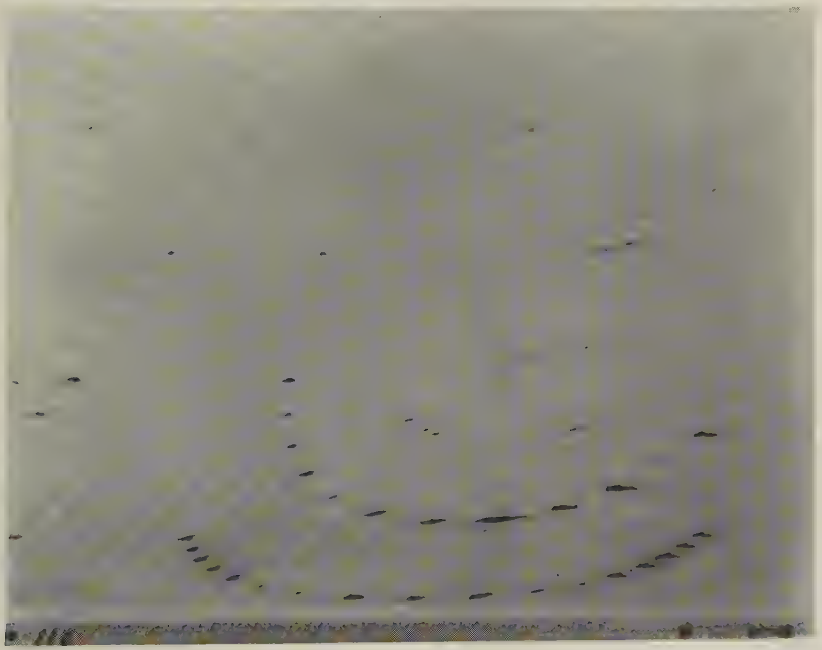


Fig. 5(*a*). First layer Weissenberg photograph.
Rotation about [110] for area with 2V = 3°.

x-ray symmetry, based on the symmetry of the individual Weissenberg patterns, was C_{2h} or D_{3d}. If the differences in diffuseness between Weissenberg patterns are neglected, a threefold axis is demonstrated and the Laue symmetry is D_{3d}. If, as we prefer, the optic axial angle of 12° is not ascribed to strain and the differences in diffuseness are not neglected, the Laue symmetry must be taken as C_{2h} with the structure very close to trigonal.

Fig. 5(*b*). First layer Weissenberg photograph.
Rotation about [100] for area with 2V=3°.

If β is exactly 90° and the lattices of single muscovite layers are exactly trigonal, Weissenberg pictures about [*hk*0] of a muscovite crystal twinned on composition plane (001) would consist of patterns of the untwinned parts exactly superposed with no doubling or diffusing of spots and with no extra spot positions. The only effect of twinning on the pictures would be a superposition of spots and an averaging of the intensities so that dissimilarities between patterns around such axes at 120° to each other would be minimized and, with equal amounts of twins at all 60° angles, dissimilarities would be eliminated. Actually the differences found in the Weissenberg photographs made at angles of 60° were very slight for fragments with larger 2V as well as with small 2V. The amount of diffuseness along (h,k,l) curves was small compared to that shown by some micas described by Hendricks. There was much more diffuseness not along (h,k,l) curves due to distortion (the corrugation) which appeared on the Weissenberg films mainly as streaks parallel to the rotation axis.

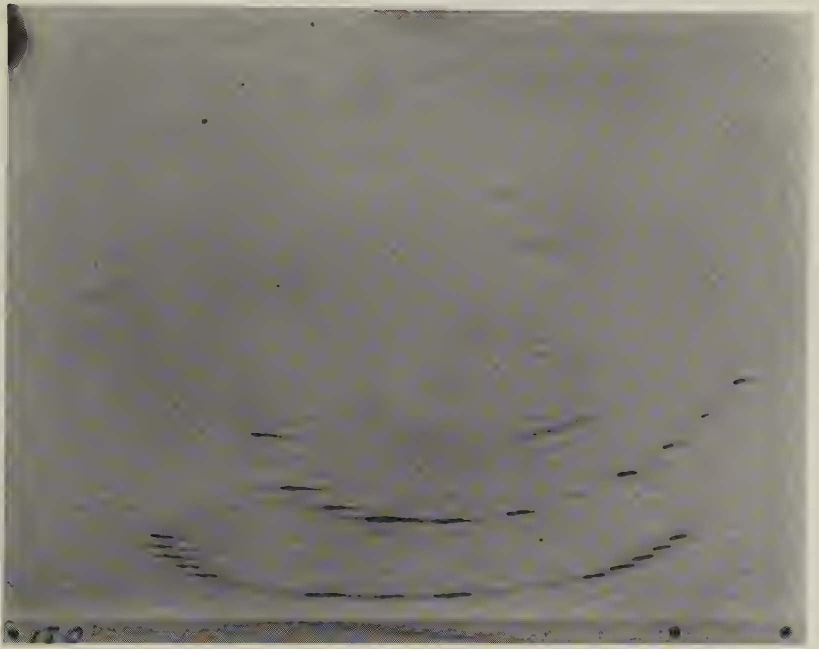


FIG. 5(c). First layer Weissenberg photograph.
Rotation about $[1\bar{1}0]$ for area with $2V=3°$.

Such distortion or diffuseness would be evident in a Laue pattern as asterism and probably accounts for most of the asterism found on the Laue photographs.

Indexing of the patterns showed all reflections with $h+k$ odd were absent, $(00l)$ with $l\neq 3n$ was absent, and only a few weak reflections for $(h\ 3n\ l)$ with $h+l=3n$ were present. For a hexagonal description, these criteria would become: K is not a fraction; for $(00L)$, $L=3n$; and for $H+K=3n$, almost all $H+L=3n$; but they would not include that $H-K+L=3n$. Also the twofold axis is parallel to the shortest identity distance in the cleavage plane.

If the mica were described as trigonal, the cell dimensions would be the same as for the monoclinic description. The possible space groups would be the enantiomorphic pair $D_3^3-C3_112$, and $D_3^5-C3_212$, the same as found by Hendricks for three-layered phlogopite and lepidolite.

For the monoclinic description there can be no threefold axis but the packing of layers may be described as simple translation of one layer with respect to the next, as from u, v, w, to $u+\frac{1}{3}$, $v+\frac{1}{3}$, $w+\frac{1}{3}$, to $u+\frac{2}{3}$, v, $w+\frac{2}{3}$, back to u, v, $w+1$. This would be equivalent to a threefold screw axis through $u+\frac{1}{3}$, $v+\frac{1}{9}$ for undistorted hexagonal mica sheets, and similarly preserves the twelvefold coordination of the potassium ions and the structure of the mica layers. The possible monoclinic space groups are C_s^3-Cm, C_2^3-C2, and C_{2h}^3-C2/m. Only C_2^3-C2 is a subgroup of the possible trigonal space groups and is therefore taken as the most probable space group. The cell dimensions are:

$a=5.20\pm.01$ Å
$b=9.03\pm.01$ Å
$c=30.04\pm.03$ Å
$\beta=90°\pm10'$

SUMMARY

Muscovite shows the same type of polymorphism as the other micas. The muscovite from Sultan Basin has a three-layered monoclinic structure with a small degree of randomness in the packing of the layers and belongs to the mica group of the second class with $Z=a$. The optic axial angle is smaller than for the commoner two-layered muscovite and variable over a flake. The variation is explained as resulting from superposition or penetration of twins based on the common mica twin law.

ACKNOWLEDGMENTS

The writers are especially indebted to A. C. Waters who collected the sample for the study and furnished the description of the occurrence.

The writers thank K. J. Murata for the spectrographic work and P. G. Nutting for the thermal dehydration curves of the micas. The writers also thank C. S. Ross. W. T. Schaller, G. T. Faust, R. E. Stevens, and R. S. Cannon, Jr. for the many informal discussions in connection with this work.

PARAGENESIS OF THE GARNET AND ASSOCIATED MINERALS OF THE BARTON MINE NEAR NORTH CREEK, NEW YORK

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ABSTRACT

The paragenetic sequence of the minerals of the Barton garnet mine shows that the crystallization of the mine rock started with the formation of a hornblende-diorite matrix and ended essentially with the crystallization of the large garnet grains and/or crystals within the hornblende rims. These rims or envelopes, which were formerly considered "reaction rims," are paragenetically earlier than the enclosed minerals. The hornblende envelopes and the minerals within the envelopes developed from retained isolated pegmatitic or deuteric solutions having more-or-less spherical outlines enclosed within the hornblende diorite. The crystallization of these isolated solutions produced first the hornblende envelopes followed by terminated crystals of hornblende and hypersthene, large grains of plagioclase, and intergrowths of hornblende and feldspar growing from the inside of the envelopes toward the center. The last mineral to form in any quantity was garnet, which covered the minerals attached to the interior of the envelopes and which also enclosed crystals of biotite, apatite, hypersthene, and rounded grains of pyrite which developed contemporaneously with the garnet.

There is no evidence of late introduction of material or of metasomatic action between any of the minerals present.

The term *deuterocryst* is proposed to apply to those crystals or large grains as hornblende, hypersthene, biotite, and garnet which developed from late pegmatitic or deuteric solutions retained within the parent rock. Such crystals are late in development in contrast to phenocrysts which appear early and are retained as conspicuous crystals or grains.

INTRODUCTION

The garnet deposits in the vicinity of North Creek, New York, are well known on account of their occurrence and economic importance. They have been frequently mentioned and briefly described in the literature.

The writer has examined the very interesting Barton Mine on Gore Mountain at intervals since 1920 and during the many visits he has searched the broken ore and quarry faces for critical evidence on the origin of the conspicuously large garnets and their hornblende rims. During the summer of 1947 additional new and important facts bearing on the paragenetic sequence of the garnet and associated minerals were discovered.

PREVIOUS WORK IN THE AREA OF THE MINE

Descriptions of the geology in the vicinity of the Barton garnet deposit, formerly called the Moore or Rogers Mine, have been presented by Miller (1, 2) and Krieger (3). None of the previous writers has given a detailed description of the order of crystallization of the garnet and associated minerals of the hornblende-rich diorite.

Concerning the geology of the mine and the immediate vicinity, Krieger (3, p. 109) states that:

> The garnet-rich rock occurs as a narrow, lens-like mass about three-fourths of a mile long with a nearly east-west strike. It varies from 50 to 300 feet in width. It is in contact on the south side with syenite, on the west end with Marcy anorthosite, on the north with gabbro and Whiteface type anorthosite. The foliation of the syenite dips about 15° to the north. The contact between the syenite and mineable garnet is nearly vertical, sloping but slightly to the north.

Miller (1, pp. 499–500) states that the

> garnets occur in lenses of Grenville sediments which were caught up or included in the great igneous masses at the time of their intrusion, the tremendous heat and pressure being especially favorable for a very complete rearrangement and crystallization of the masses (inclusions) of sediments which were pretty low in silica. . . .
>
> The hornblende rims or envelopes are quite certainly great reaction rims around the garnets, but just at what stage of the metamorphism they were produced is not at all clear to the writer. The rounded character of the garnets shows pretty clearly that the rims of hornblende are of secondary origin and that they were formed sometime after the crystallization of the garnets and possibly at the time when the pressure producing the foliation of the rocks was brought to bear.

Miller (2, p. 406) modified his previous theory. He says that

> before the intrusion of syenite magma, the southern border portion of the body of gabbro (probably metagabbro) was more or less intimately cut and assimilated by the anorthosite magma, producing a synthetic rock rich in fairly large garnets without hornblende envelopes, . . .
>
> By metamorphism, induced by the rise of the great body of quartz syenite magma, the mine rock, with its large hornblende-enveloped garnets was produced along the southern side of the body of gabbro. . . . The composition of the mine rock indicates that little if any material was added to the gabbro by the syenite magma, and so the nature of the metamorphism was largely or wholly dynamothermal, . . .

As the previous studies on the garnet deposits of the area have been devoted to the broader aspects of the problem of the genesis of the garnet-bearing rock, the writer will not further review that phase of the problem as the foregoing will suffice as an introductory background to this interesting problem.

It is the writer's belief that the answers to the broader problems lie first in the correct interpretations of the final or end stages of the process, from which the earlier and broader phases may be more readily and accurately deduced. Neither the source of the materials of the garnet-bearing diorite nor the manner in which they reached their present position with respect to the adjoining rock types will be considered at this time.

DESCRIPTION OF THE GARNET-BEARING ROCK AND ASSOCIATED MINERALS

The mine rock is a dark-gray medium to coarse-grained hornblende-rich diorite containing large dark-red garnets surrounded by coarse-grained hornblende rims. In narrow zones along the north and south borders of the deposit the garnets are smaller and do not possess the conspicuous hornblende rims. The composition of the diorite, away from the garnet and associated minerals, as determined from eight thin sections of average-appearing diorite is approximately 29% plagioclase, 56% hornblende, 13% hypersthene, 1% biotite; a little pyrite, apatite and magnetite are also present. According to Johannsen's classification the rock is a meladiorite (3212). The minerals of the matrix are unusually fresh; however, there is a slight peripheral alteration of some hornblende grains to chlorite and magnetite. The alteration products amount to 5.5% and are computed as hornblende. The larger garnets have thicker envelopes in which the *hornblende* grains are often 1½ to 2 inches across the cleavage faces. Most of the hornblende is xenomorphic granular. Near the garnet it occasionally forms radial intergrowths with the plagioclase feldspar. The intergrowths terminate with spherical surfaces against the

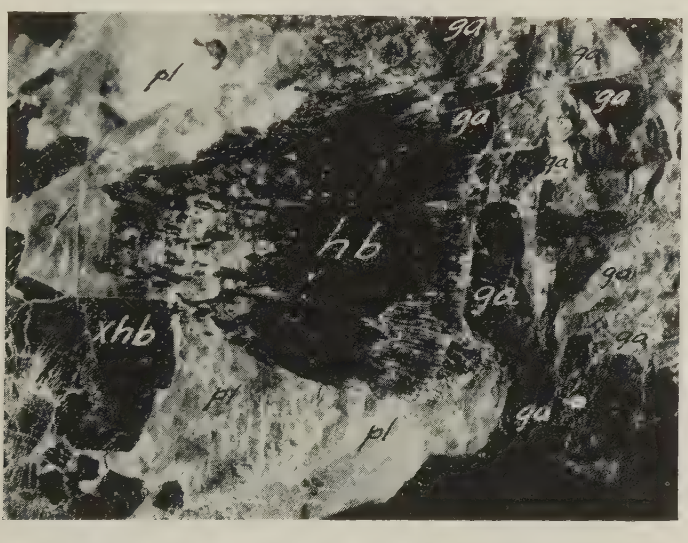

FIG. 1. A radial intergrowth of hornblende (hb) and plagioclase (pl) growing from the hornblende rim toward a large garnet grain (ga). The crystals of hornblende (xhb) of the rim are oriented with their terminal ends toward the garnet. They are covered with feldspar (pl). The sequence of mineral development is hornblende, feldspar, and then garnet, which is the last important mineral to crystallize. × = 2.0.

garnet grains. Some terminated crystals of hornblende are occasionally present in association with plagioclase which covers the terminations and occupies a space between the terminal faces and the garnet, Fig. 1.

The only feldspar observed was *plagioclase* which has a composition between Ab_{55} An_{45} and Ab_{50} An_{50} in the diorite matrix between the large garnet grains. The grains of plagioclase, several inches across the cleavage faces, which occur next to the garnets as segments of the envelopes have a composition about Ab_{65} An_{35}. The feldspar had the longest period of crystallization. It appeared early as irregular grains in the diorite matrix and also late as masses in the envelopes and as fillings in some of the wider fractures in the garnet and in the minerals of the rims. The larger grains of plagioclase are rather clear and glassy.

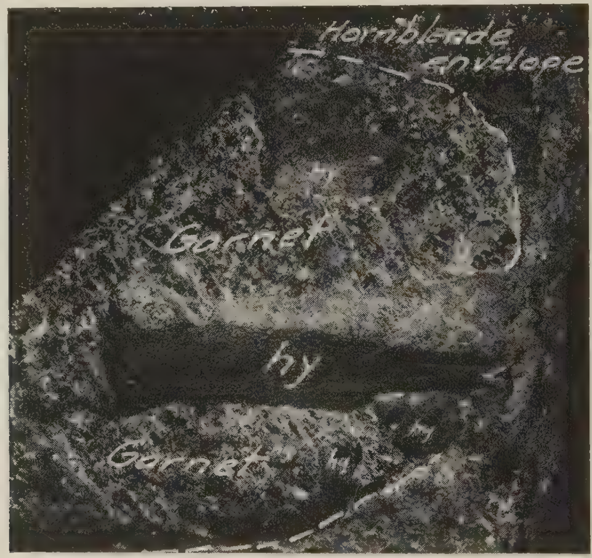

FIG. 2. A large garnet grain with a large crystal of hypersthene (hy) growing into the garnet from the hornblende rim. A number of smaller hypersthene crystals are also present and some of these are apparently surrounded by garnet which is outlined from the hornblende rim by the broken line. The large crystal is 4 inches long.

The *hypersthene* also had a relatively long period of crystallization. It occurred early as small interstitial grains in the diorite matrix where the pink-brown color of the mineral makes its recognition easy with a binocular microscope. The examination of the diorite specimens reveals the fact that the amount of hypersthene present varies greatly from one sample to another. In some of the hornblende envelopes the hypersthene is more abundant than in others. In the outer parts of the envelopes it retains its interstitial position between the hornblende grains. In the inner portion of the envelopes the hypersthene at times becomes relatively abundant, and in certain instances crystals up to 4 inches long Fig. 2, have grown from the inside of the envelope and developed terminated crystals that extend *centripetally* into the garnet. Essentially euhedral crystals of hypersthene up to 3 inches in length occur completely within the garnets, Fig. 3. A few small, well-developed, fresh crystals were also found as inclusions within the glassy feldspar between the hornblende of the envelopes and the garnet.

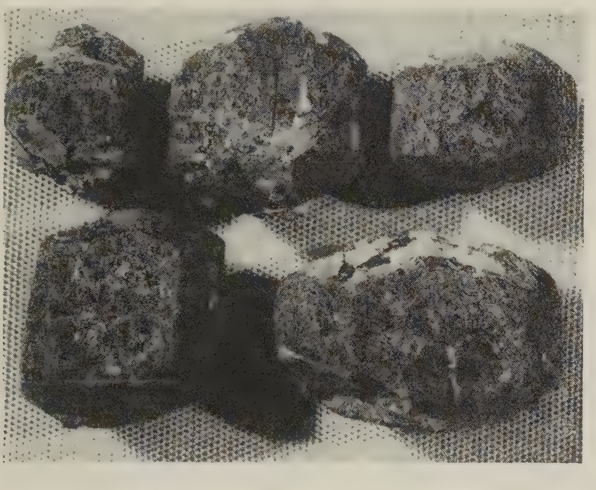

Fig. 3. Crystals of hypersthene which occur completely within the garnet grains. ×=1.4.

Some of the hypersthene crystals in or near the feldspar and/or hornblende of the envelopes are considerably altered to chlorite and serpentine along fractures and cleavage planes. The hypersthene grains in the hornblende-feldspar matrix are fresh and unaltered even though the hornblende in contact with it may be slightly altered along the grain boundaries as described above.

The large, brilliant red *garnet* grains and crystals are the most spectacular and interesting mineralogical feature of the deposit. Their average size runs from four to six inches while garnets up to a foot in diameter are not uncommon. Krieger (3, p. 113) states that "garnets three feet in diameter and yielding about one and one-half tons of garnet have been taken out." Crystal faces as a rule are absent although a few individuals with rough dodecahedral forms are at times present even on the larger garnets. Each mass of garnet, regardless of size, appears to be a single crystalline unit and not a granular aggregate. This supposition is supported by two criteria: first, and most convincing is the presence of dodecahedral faces on a few of the larger pieces, and second, all grains, large and small, have more or less continuous fractures with even to conchoidal surfaces extending across the grains. Many small cross fractures with conchoidal surfaces are also present. The garnet fragments have the shape of very rough rectangular parallelopipeds instead of rounded subhedral grains as is not uncommon in garnet deposits in which the garnet masses consist of many small irregular grains.

Biotite is the commonest inclusion in the garnet. Irregular black crystals up to an inch in length and having rough and uneven crystal faces are not uncommon. Segments of coarse granular biotite occur sparingly in the envelopes next to the garnet. The biotite inclosed in the garnet, and most of that occurring in the envelopes, is of a deep brown color by transmitted light; however, occasional laminae of a bright green biotite occur interlaminated with sharp contacts with the brown variety in the envelopes. The birefringence in each case is the same. Only a relatively small amount of biotite occurs in the diorite matrix.

Small yellow transparent crystals of *apatite*, less than $\frac{5}{8}''$ long, occur as inclusions in the garnets usually near the contact with the envelope minerals. The crystals are occasionally doubly terminated and have rounded edges between the crystal faces. The apatite sometimes occurs in the hornblende or hypersthene. It is never abundant except in very small portions of the garnet.

Pyrite in small amounts is common in the diorite, hornblende envelopes, and as inclusions in the garnet. It also occurs as thin films in the fractures through the garnet and envelope minerals. As inclusions it always occurs as small rounded or irregular masses. Crystals were at no time observed. When the thin films in the fractures of the garnet were loosened the impressions of the conchoidal fractures could be clearly seen with a binocular microscope. The films of pyrite in fractures along the basal cleavage of the plagioclase show, in like manner, the impressions of the twinning striations which were molded onto the pyrite film.

Chlorite, serpentine and *magnetite* occur sparingly as alteration products of hornblende and hypersthene.

A little *calcite* is present along the fracture planes in the garnet and envelope minerals.

Two unknown minerals in very small amounts were observed. One occurs with pyrite, or alone, as thin films in fractures in the garnet and envelope minerals while the other forms the walls for a few very small crystal cavities of an unknown mineral.

Paragenesis of the Minerals

The structural, textural and mineralogical relationships previously described suggest that the progress of crystallization was from the medium-grained hornblende-feldspar matrix toward the coarse-grained hornblende envelopes, and ended with the large garnet grains and/or crystals. The coarse-grained envelopes of hornblende, feldspar, biotite and hypersthene, together with the garnet, represent a deuteric,* or in reality a retained *pegmatitic phase* of the diorite. Had this material accumulated in a fissure and crystallized under similar conditions a basic garnet-rich hornblende pegmatite would have undoubtedly resulted.

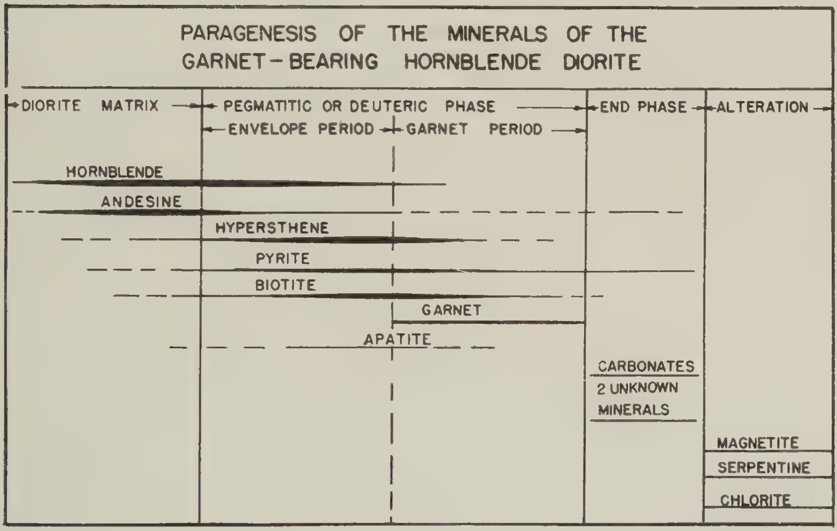

Fig. 4. Diagram showing the continuous and uninterrupted phases in the paragenesis of the garnet-rich hornblende diorite of the Barton Mine on Gore Mt., New York.

The paragenetic sequence of the minerals of this garnet-rich hornblende diorite is shown diagrammatically in Fig. 4. Crystallization began with the contemporaneous formation of hornblende and plagioclase feldspar which developed the xenomorphic mosaic of the ground mass or matrix. In addition, small amounts of hypersthene, pyrite, and biotite appeared interstitially between the hornblende and plagioclase.

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* For the crystals, as hypersthene, biotite, garnet, apatite, and the terminated hornblende crystals which have been described above as having developed from late or deuteric solutions retained within the body of the rock, I propose the name *deuterocrysts*. Such crystals are late to develop as contrasted with phenocrysts which appear early and are retained as prominent or conspicuous crystals or grains.

The initial phase of crystallization began at essentially the same time throughout the mass of the mine rock resulting first in the formation of the solid matrix with the scattered, isolated, still unconsolidated phase consisting essentially of the envelope minerals, garnet and such materials which remained in the residual solution due to their low melting point or high solubility. These have been aptly called "fugitive constituents" by Shand (4, p. 34).

At the close of the matrix stage the andesine had become nearly exhausted and the remaining plagioclase in solution had become enriched in the albite molecule by the removal of the more calcic andesine. The crystallization of the substances in the late phase, or deuteric solutions, started the second or pegmatitic phase with the development of the coarse-grained hornblende envelopes in contact everywhere with the matrix. In this stage the crystallization was distinctly *centripetal*, that is, the crystallization progressed toward the center of the residual isolated solution confined in more-or-less spherical masses within the already solid matrix. The situation is not unlike the crystallization of a filled-fissure vein or a pegmatite dike, in which the direction of crystallization is toward the center of the vein or dike. The difference is chiefly in the shape of the retaining walls. In pegmatite dikes and other tabular vein-like mineral deposits the terminated minerals extend from the walls or centers of support in the direction of their growth. Likewise in the hornblende envelopes the minerals that are terminated have their terminations directed toward the center. In chemistry the process of separating subtances by crystallization of the less soluble ones from a common solution is called fractional crystallization. The hornblende remaining in the pegmatitic or deuteric phase was removed by his process of fractionation during the formation of the envelopes, leaving a residual solution confined within the envelopes consisting chiefly of garnet with some hypersthene, pyrite, biotite, andesine, calcite and possibly minor amounts of other carbonates. Small amounts of fine-grained materials not determined and also small amounts of the fugitive constituents invariably associated with silicate solutions were also undoubtedly present.

In addition to the rock containing hornblende-rimmed garnets, two additional types of garnet-bearing hornblende diorite are present in the mine. The most abundant of the two occurs in a zone along the north side of the deposit. It is similar to that of the main body of diorite but contains numerous small garnets up to an inch or two in diameter but without the prominent hornblende rims. The total amount of hornblende and plagioclase feldspar appears to be nearly the same but at the end of the crystallization of the matrix there was not an accumulation of a hornblende-garnet-rich pegmatitic phase. There is, however, a hornblende-feldspar intergrowth along the periphery of many of the garnets similar to the intergrowths around the large ones that are hornblende-rimmed. Except for the envelope minerals and the inclusions in the large garnets already described, the paragenesis of this phase is the same.

Another less common and more irregularly distributed type of garnet-bearing rock in the mine consists essentially of an irregular, granular aggregate of hornblende, hypersthene, and garnet. The material is both medium and coarse-grained. It is believed to represent material belonging to the pegmatitic or deuteric phase which had accumulated in considerable volume of irregular shape. The paragenetic sequence of these masses is the same as that of the hornblende-rimmed garnet masses, except that the hornblende produced a granular slush-structure throughout the mass instead of developing rims or envelopes. Both hypersthene and garnet occupy the interstitial spaces between the hornblende grains.

The mine manager, Charles Barton, stated that a "vein of garnet" at one time appeared in one of the quarry faces. An occurrence of this kind would be expected in the event a fracture developed at a time when and where the late garnet solution could fill it.

SUMMARY OF EVIDENCES SUPPORTING THE PARAGENETIC RELATIONSHIP DESCRIBED ABOVE

1. The shift in the composition of the plagioclase feldspar from Ab_{50} in the matrix to Ab_{65} for the large grains in the envelopes and in contact with the garnet shows that the matrix is earlier.

2. The greatly increased size of the mineral grains in the envelopes compared with that of the minerals in the matrix indicates a late stage of crystallization in the presence of a greater amount of mineralizers.

3. The presence of hornblende-feldspar and biotite-feldspar intergrowths in the zone next to the garnet indicates a eutectic-like phase of these minerals and a late phase of their development.

4. The radial intergrowths of hornblende and feldspar (Fig. 2) indicate that they grew centripetally from the interior of the hornblende envelopes toward the garnet.

5. The subhedral hornblende oriented with its terminal faces directed toward the garnet indicates that the direction of growth of the hornblende on the inside of the envelopes was toward the garnet centers.

6. Hypersthene, a late interstitial mineral in the matrix, becomes more abundant interstitially in some of the envelopes. When the amount of hypersthene in the envelopes is large, it frequently develops large crystals projecting from the inside of the hornblende envelopes into the garnet which shows unmistakably the direction of crystal growth. The last of the hypersthene developed contemporaneously with the garnet

and produced euhedral crystals attached to the simultaneously crystallizing garnet which completely enclosed the hypersthene crystals.

7. The sequence of crystallization of hypersthene from interstitial grains in the matrix to euhedral hypersthene in the garnet indicates an important series of events in the paragenesis of this mineral which shows its crystallization to have started in the matrix and ended with the euhedral "deuterocrysts" in the garnet.

8. The occurrence of coarse-grained masses of biotite, a hydrous mineral, in large grains next to the garnets as segments of the hornblende envelopes indicates a late stage for the crystallization of the envelopes.

9. The increasing amount of pyrite, occurring as rounded inclusions, in hornblende, hypersthene, feldspar, and garnet, and also as films filling narrow fractures in the garnet and the associated minerals of the envelopes indicates that the coarse-grained envelopes and the inclosed minerals were the last to crystallize.

10. Films of pyrite, feldspar, and other minerals in the garnet fractures show casts of the conchoidal fractures, and the pyrite in the fractures of the plagioclase masses near or in contact with the garnet, frequently shows casts of the twinning striations when occupying fractures along the basal cleavage. This relationship shows conclusively that the last substances to solidify simply filled the fractures without reacting with the wall materials, and that the introduction of new materials or the reworking of earlier minerals by metasomatic processes had not occurred.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Mr. Charles Barton, Mine Manager, for the privilege of examining the garnet deposit and to Dr. William J. Miller of the Department of Geology, University of California for reading the manuscript.

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THE LABORATORY GROWTH OF QUARTZ

I. I. Friedman[1]

Abstract

The lack of a supply of domestic quartz suitable for piezoelectric applications has stimulated interest in methods of synthesis.

The system H_2O-SiO_2-Na_2O was chosen for investigation. Data are presented giving the solubility of quartz in sodium hydroxide solutions from 1% to 13% Na_2O at temperatures from 250° to 450° C. The solubility rate and rate of quartz growth from these solutions was determined. The large growth rate led to successful attempts at laboratory synthesis. A discussion is given of several growth techniques.

The use of quartz as a frequency controlling element in radio and radar circuits has increased to the extent that almost 10,000,000 units were used during the final year of the last war. The raw material for this purpose must be fairly free from optical twinning, as well as from electrical (dauphiné) twinning. Brazil is the main source of suitable material. The possibility of the loss of this source due to either enemy action or through depletion has initiated research for quartz substitutes as well as for methods of synthesis of quartz. The success which has been achieved in the synthesis of large single crystals of a great variety of materials, has prompted interest in the synthesis of quartz crystals suitable as raw material for piezoelectric use. Late in 1945 the author began a consideration of this problem.

Previous workers[2,3,4] have grown quartz by what might be called "trick" methods, such as convection transport, differential "solubility" of the different forms of silica, etc. The writer, having had some experience in growing water soluble materials such as ammonium dihydrogen phosphate, lithium sulfate monohydrate, iodic acid, etc., reasoned that quartz could be grown by these proven methods.

The method which was decided upon was first to find a system where quartz would be the primary crystalline phase, and one in which quartz would be:

(*a*) sufficiently soluble and
(*b*) supersaturate sufficiently to make the method practical.

A suggestion of Morey and Ingerson led the author to investigate the H_2O-Na_2O-SiO_2 system. Temperatures from 250° to 450° C. were investigated.

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[1] Present address: Department of Geology, University of Chicago, Chicago 37, Illinois.

[2] Kerr, Paul F., and Armstrong, Elizabeth, *Bull. Geol. Soc. Am.*, **54**, Suppl. 1, 1–34 (1943).

[3] Spezia, G., *Accad. Sci. Torino, Atti*, **44**, 95–107 (1908).

[4] Nacken, R., "Report on the Research Contract for Synthesis of Oscillator Crystals," Captured German Report RDRDC/13/18.

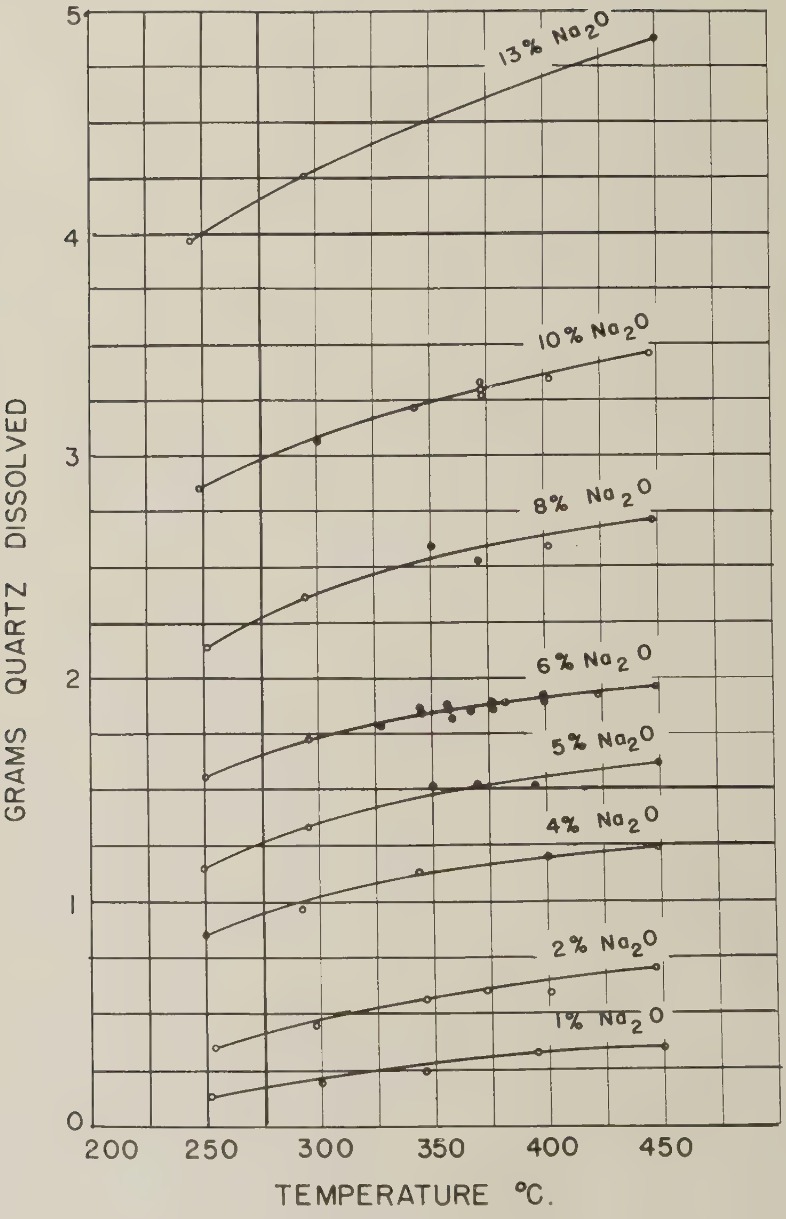

FIG. 1. Concentration in wt.%

After the work had progressed to the point where it could be evaluated, the reports of Nacken's work in Germany during the war[4] became available. Several inaccuracies in this research, plus the conviction that the German method was impractical and basically unsound from a crystal growing standpoint, prompted me to continue. Subsequent attempts of several laboratories in this country to put the German method into practice, with generally negative results, have strengthened this viewpoint.

Experimental

The solubility of quartz was determined by observing the loss in weight of a quartz block in contact with NaOH solution for a given temperature and concentration. A weighed block of quartz was placed in an 18 ml. high pressure bomb, 10 ml. of sodium hydroxide solution of known concentration was pipetted into the bomb and the bomb sealed. It was then placed in an electric furnace and equilibrated at a definite temperature. The whole apparatus was slowly rocked to provide agitation. A description of the apparatus will be found described by Tuttle and Friedman.[5] After heating for from 8 to 120 hours, the bombs were removed from the furnace and quickly quenched under a cold water tap. They were then opened and the remainder of the quartz block was washed, dried and weighed. The solubility of quartz in sodium hydroxide solutions is shown as a function of temperature in Fig. 1.

In order to determine whether the data represented equilibrium values, the rate of solution of quartz was also determined. For this purpose uniform quartz blocks cut parallel to the second order prism $(11\bar{2}0)$ 2.5 cm. × 1.5 cm. × 0.25 cm. were used. The results for two sodium hydroxide concentrations are given in Fig. 2.

In any synthesis of quartz, the rate of growth will determine the practicability. To determine the approximate rate of growth, runs were begun as before, using the above "X" cut quartz blocks. However, instead of quenching when equilibrium was reached, the furnaces were slowly cooled at a known rate. After cooling through 25° C., the bombs were quenched as before. The rate of cooling was decreased until the maximum amount of quartz re-deposited, as determined from the solubility curves (Fig. 1). The results are given in Fig. 3. The tendency of quartz to supersaturate in sodium hydroxide solutions prevents spontaneous "snow storms" of small crystals when the rate of cooling is in excess of the maximum equilibrium rate.

The dropping off of the growth rate below 300° C. will fix the lower temperature limit of any commercial growth process using these com-

[5] Tuttle, O. F., and Friedman, I. I., *J. Am. Chem. Soc.*, **70**, 919 (1948).

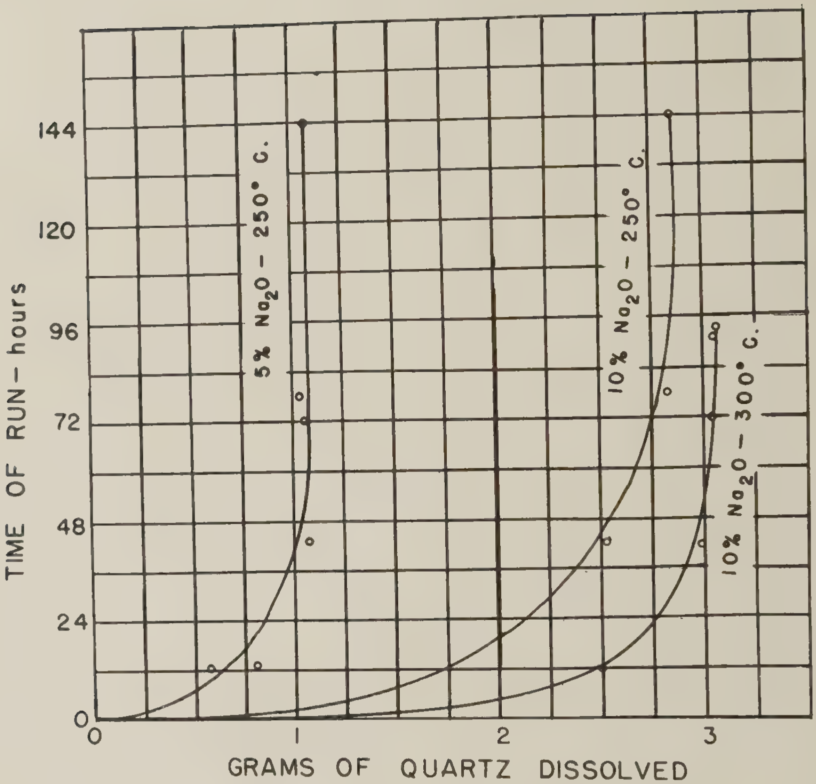

FIG. 2

positions. The upper limit is fixed by the α-β inversion at 573° C. Quartz cooled through the inversion will become electrically twinned, unless very special methods are employed of applying stress to the crystal as it passes through the inversion. Actually, a somewhat lower temperature than the inversion temperature may be desirable due to the temperature-pressure limitations of large scale equipment.

The greater the concentration of sodium hydroxide, the larger the quartz yield per run in a batch method. However, the viscosity of the high Na_2O-SiO_2 concentrations will slow down diffusion and cause growth difficulties.

The liquid immiscibility observed in this system[5] introduces another factor which has a bearing on crystal growth. The author has observed that the growth on a quartz plate immersed in both phases is mainly upon the surface of the quartz plate which is in contact with the "heavy" (lower water content) phase. The rate of solution and redeposition will probably differ in the two phases. There is some experimental evidence to show that solubility takes place more rapidly in the "lighter" phase, and deposition more rapidly from the "heavier" phase. It might, therefore, be possible to suspend quartz fragments in the light phase, and immerse quartz "seeds" in the heavy phase. Oscillating the temperature should then cause quartz to migrate from the fragments to the seed.

As a check on the practicability of quartz growth from the H_2O-Na_2O-SiO_2 system, a water glass containing 20% Na_2O, 64% SiO_2, 16% water (Philadelphia Quartz Company—"G" brand sodium silicate) was used as a starting material. 5.0 grams of the "G" brand sodium silicate was placed in an 18 ml. bomb, 10 ml. of water pipetted in, a quartz seed added and the bomb sealed. The solution was saturated with respect to quartz at approximately 450° C. The bombs were then heated to 325° C. and allowed to equilibrate at that temperature for thirty hours while being continuously rocked. They were then rapidly cooled (100°/hour)

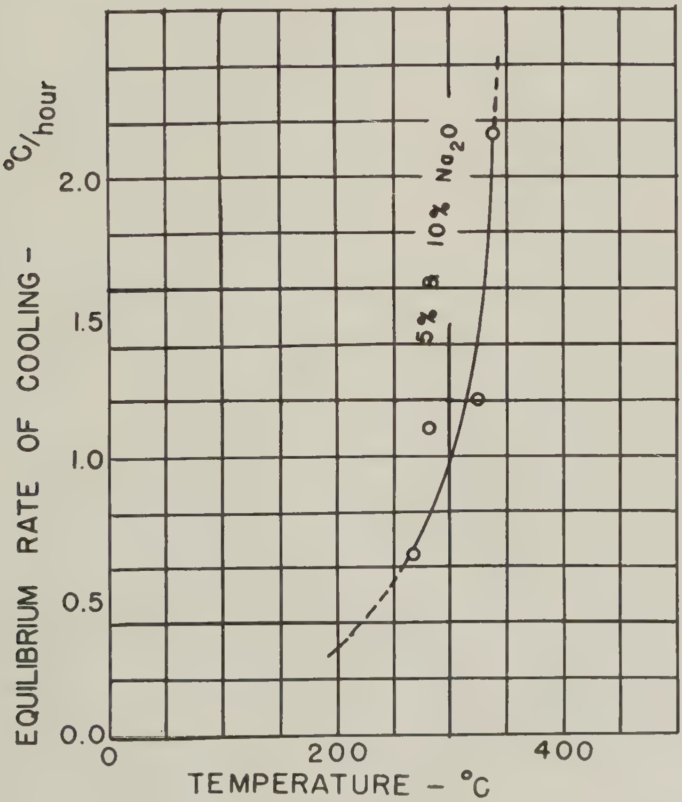

Fig. 3

to room temperature and opened. In every run the seed gained from 0.25 to 0.3 grams.

In a few cases five or six consecutive runs were made using the same seed. There is no veil or other line of demarkation to mark the boundaries of each run. The growth was remarkably good, even as compared to certain easily grown materials such as alum or Rochelle salt.

With the exception of two seed plates cut parallel to the major rhomb $(10\bar{1}1)$, all the seed plates used were cut parallel to the second order prism $(11\bar{2}0)$.

The (1120) plates developed rhomb ($10\bar{1}1$ and $01\bar{1}1$) and first order prism faces. Most of the growth was in a direction of the minor $(01\bar{1}1)$ and major $(10\bar{1}1)$ rhombs. The use of seeds cut parallel to the minor rhomb resulted in nearly all growth taking place on the large $(01\bar{1}1)$ surface. The growth rate should be greater with seeds so oriented, since the direction of fastest growth in natural quartz is normal to the minor rhomb $(01\bar{1}1)$ faces, closely followed by the rate normal to the major rhomb $(10\bar{1}1)$ face.

The author wishes to acknowledge the aid given to him by Dr. O. F. Tuttle who helped initiate this research project and is responsible for many of the ideas embodied herein. A great debt is also owed to Mr. Charles Jackson for his assistance in carrying out the experimental work.

X-RAY STUDY OF HOLDENITE, MOOREITE AND TORREYITE

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ABSTRACT

The following data have been obtained by the Weissenberg and powder diffraction methods:

Holdenite. Unit cell dimensions: $a_0=11.97$kX, $b_0=31.15$, $c_0=8.58$. Space group *Bmam*. Cell contents $2[(Mn, Ca)_{25}(Zn, Mg, Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}]$. Specific gravity 4.118 (calc.), 4.11 (meas.).

Mooreite. Unit cell dimensions: $a_0=11.18$ kX, $b_0=20.25$, $c_0=19.52$. Space group $P2_1/m$. Cell contents $13[(Mg, Mn, Zn)_8(SO_4)4H_2O]$. Specific gravity 2.543 (calc.), 2.47 (meas.).

Delta-mooreite, originally thought to be a chemical variant of mooreite, is a distinct species. The new name *torreyite* is proposed for the mineral.

HOLDENITE

Holdenite was first described by Palache and Shannon[1] in 1927, as an arsenate of manganese and zinc with the probable formula: $Mn_8Zn_4(AsO_4)_2(OH)_{10}O_4$. The only specimen on which the mineral was found is a slab of massive franklinite apparently from the wall of a veinlet as indicated by a slickensided surface. Also on the specimen were small amounts of calcite, willemite, barite, galena, and pyrochroite.

The orthorhombic crystals are all well developed with many forms, and conform to dipyramidal symmetry. The crystals are tabular parallel to the macropinacoid and have a poor brachypinacoidal cleavage. The color varies slightly but is mostly a clear pink with either a yellowish or purplish tinge. Crystals from the original specimen have been studied by the Weissenberg method. 0-layer photographs were taken in copper radiation about [001], [010], and [100], and 1- and 2-layer photographs were taken around [001]. The following data were obtained:

(a) from rotation photographs	(b) from Weissenberg photographs
$a_0=11.84\pm0.2$ kX	$a_0=11.97\pm0.08$ kX
$b_0=31.15\pm0.3$	$b_0=31.15\pm0.08$
$c_0=8.58\pm0.3$	$c_0=8.58\pm0.1$

The original morphological cell selected by Palache coincides with the structure cell here found. Using the values from Weissenberg photographs the axial ratio of the structure cell is: $a_0:b_0:c_0=.3842:1:.2754$ as compared with $a:b:c=.3802:1:.2755$ in the morphological cell. The cell of holdenite as determined from the Weissenberg projections is

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 305.

[1] Palache, C., and Shannon, E. V., Holdenite, a new arsenate of manganese and zinc, from Franklin, New Jersey: *Am. Mineral.*, **12,** 144–148 (1927).

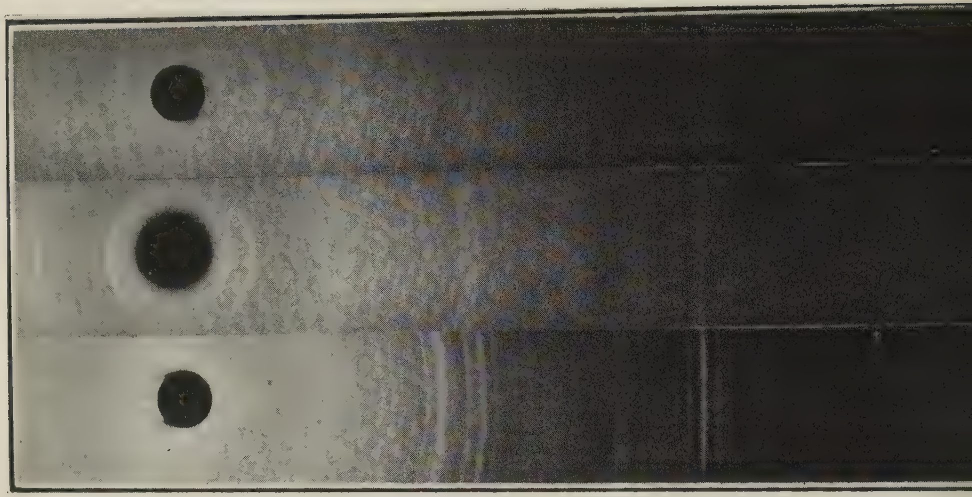

FIG. 1. Powder Photographs
Top: mooreite
Middle: torreyite
Bottom: holdenite

B-centered with a glide along [100]. Assuming that the mineral is holohedral as indicated by its morphology, the space group is *Bmam*. The spacing data obtained from powder photographs is summarized in Table 4, and the pattern is shown in Fig. 1.

The specific gravity was originally given as 4.07, which was determined by floating in Clerici solution. By measurement on the Berman microbalance it has been redetermined as $4.11 \pm .01$. Using this data and the original analysis of Shannon the following cell contents have been obtained:

The simplest formula is thus: $(Mn, Ca)_{25}(Zn, Mg, Fe)_{15}(AsO_4)_7(OH)_{33}$-$O_{13}$ with $Mn:Ca=46:4$, and $Zn:Mg:Fe=25:3:2$.

The calculated specific gravity is 4.118, which compares closely to the measured specific gravity of 4.11. The formula is complex and can not be regarded as entirely certain due to the unsatisfactory nature of the analysis. The original sample, obtained after great difficulty, weighed only 0.42 gram, and was shown to contain impurities in unknown amounts. Almost 10 per cent of the sample was assumed to be impurities, but there is no tangible evidence to that effect. Perhaps some of the silica is present substituting for arsenic, rather than all in the form of willemite. Further, more calcium may be substituting for manganese than is indicated, since the actual amount of carbon dioxide present is uncertain.

TABLE 1. CELL CONTENTS OF HOLDENITE

	1	2	3	4	5	6		7	8
CaO	3.80	.268	.0478	.0478	.0478	3.81			2.81
							50.93	50	
MnO	37.75	41.92	.5910	.5910	.5910	47.12			40.84
ZnO	28.08	25.12	.3087	.3087	.3087	24.61			25.46
MgO	1.45	1.61	.0399	.0399	.0399	3.18	30.00	30	1.51
FeO	1.80	2.00	.0278	.0278	.0278	2.21			1.80
As_2O_5	17.40	19.32	.0846	.4230	.1692	13.49			20.14
H_2O	6.62	7.35	.4079	.4079	.8158	65.04		66	7.44
PbO	Trace					O=147.18		148	
SiO_2	2.01								
CO_2	[1.09]								
	[100.00]	100.00		1.846					100.00

1. It was shown that the analyzed sample was impure and contained calcite and willemite. From this it has been assumed that the silica, carbon dioxide, and their combining proportions of zinc and calcium are due to such impurities. CO_2 was shown to be present by qualitative test and is here given by difference.
2. Analysis 1 recalculated to 100 per cent after the deduction of CaO and SiO_2 as calcite and willemite.
3. Molecular quotients.
4. Atomic quotient of oxygen.
5. Atomic quotient of the metals.
6. Measured unit cell contents. Molecular weight of cell = 7973.
7. Ideal unit cell contents.
8. The ideal analysis for the formula: $2[(Mn,Ca)_{25}(Zn,Mg,Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}]$ with Mn:Ca = 46:4, and Zn:Mg:Fe = 25:3:2.

MOOREITE

The original description of this mineral was made by Bauer and Berman[2] in 1929 using material from Sterling Hill, New Jersey. The mooreite is associated with altered pyrochroite, rhodochrosite, zincite, and fluoborite in veinlets of calcite-franklinite-willemite ore. Two varieties of mooreite were recognized. One, mooreite proper, occurs in cavities in the pyrochroite in well developed tabular crystals; here the association is with fluffy fluoborite, which resembles fibrous willemite. The other type is massive and occurs in veins cutting the pyrochroite; here the fluoborite is lacking and willemite is in very close association. This latter

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[2] Bauer, L. H., and Berman, Harry, Mooreite, a new mineral, and fluoborite from Sterling Hill, N. J.: *Am. Mineral.*, **14**, 165–172 (1929).

TABLE 2. CELL CONTENTS OF MOOREITE

	1	2	3	4	5	6	7	8
MgO	25.41	25.38	.629	.629	.629	57.98		25.26
MnO	11.46	11.93	.168	.168	.168	15.49	104	11.11
ZnO	24.57	24.58	.302	.302	.302	27.84		25.19
SO_3	11.11	10.99	.137	.412	.137	12.63	13	10.72
H_2O	27.20	27.12	1.505	1.505	3.01	277.46	286	27.17
B_2O_3	present					O=278.38	286	
	99.75	100.00		3.02				

1. Original analysis of L. H. Bauer, 1929. B_2O_3 found present but not determined.
2. Analysis 1 recalculated to 100 percent after deducting $CaCO_3$ 0.89 and SiO_2 0.06 per cent.
3. Molecular quotients.
4. Atomic quotient of oxygen.
5. Atomic quotient of the metal.
6. Measured number of atoms in the unit cell. Molecular weight of the cell=9217.92.
7. Theoretical number of atoms in the unit cell.
8. Calculated analysis from the formula:

$$13[(Mg, Mn, Zn)_8(SO_4)(OH)_{14} \cdot 4H_2O] \text{ where } Mg{:}Mn{:}Zn = 59{:}16{:}29.$$

variety has been called delta-mooreite and is re-described on a following page.

The crystals of mooreite are white with a pearly luster and are tabular parallel to the cleavage, which is perfect and clinopinacoidal. Though no mention of twinning was made in the earlier description, effects seen optically and on x-ray patterns show that many of the crystals are twinned. An attempt to define the twinning law has proved unsuccessful; all evidence indicates twinning on $\{100\}$, but this is not certain.

Material was used from the type analyzed specimen from Sterling Hill. Rotation, 0-, 1-, 2-layer Weissenberg photographs were taken about [100], [010], [001]. The unit cell dimensions using the average obtained from 0-layer Weissenberg films are:

$$a_0 = 11.18 \text{ kX}, \; b_0 = 20.25, \; c_0 = 19.52.$$

The powder photograph is illustrated in Fig. 1 and the data summarized in Table 4. The space group is defined by the observed systematic extinctions,

hkl present all orders
$h0l$ present all orders
$0k0$ present only when $k=2n$,

as $P2_1$ or $P2_1/m$. Since the morphology is monoclinic holohedral the space group is $P2_1/m$. The elements and projection constants in the cell are:[3]

$$p_0=1.743 \qquad a=0.551$$
$$q_0=0.812 \qquad c=0.961$$
$$\mu=57°37' \qquad \beta=122°23'$$

The ratio of the x-ray cell is: $a_0:b_0:c_0=0.552:1:0.964$.

The specific gravity was originally given as 2.470, as measured on the pycnometer, and this was confirmed by several new measurements on the Berman microbalance. Using this specific gravity and the observed cell dimensions, the cell contents are as follows:

The simplest formula is thus: $13[(Mg,Mn,Zn)_8(SO_4)\ (OH)_{14}\cdot 4H_2O]$ where $Mg:Mn:Zn=59:16:29$. (Berman gives: $Mg:Mn:Zn=4:1:2$.) The specific gravity calculated from this is 2.543, as compared with the experimental value of 2.470.

The formula found here is identical with that given by Berman. The agreement between the actual number of atoms in the unit cell and the theoretical number and between the calculated and measured specific gravities is satisfactory in view of the large size of the cell and the presence of impurities in unknown amounts in the analyzed sample.

TABLE 3. A COMPARISON OF THE PROPERTIES OF MOOREITE AND TORREYITE (DELTA-MOOREITE)

Mooreite	Torreyite (delta-mooreite)
$(Mn, Mg, Zn)_8(SO_4)(OH)_{14}\cdot 4H_2O$	$(Mg, Mn, Zn)_7(SO_4)(OH)_{12}\cdot 4H_2O$
where $Mg:Mn:Zn=4:1:2$	where $Mg:Mn:Zn=5:3:4$
$nX=1.533$	$nX=1.570$
$nY=1.545$	$nY=1.584$
$nZ=1.547$	$nZ=1.585$
$2V=50°\pm$	$2V=40°\pm$
$G=2.47$	$G=2.665$
Perfect clinopinacoidal cleavage.	Perfect clinopinacoidal cleavage.
Monoclinic holohedral.	Monoclinic.
Powder data in Table 4 and Fig. 1.	Powder data in Table 4 and Fig. 1.

TORREYITE (formerly delta-mooreite)

Delta-mooreite was first described by Bauer and Berman[2] as a very basic, hydrous sulfate of magnesium, manganese and zinc, differing somewhat from mooreite in ratios. It also was observed to be formed

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[3] The elements given in Berman's paper were calculated from selected angles. LaForge (priv. comm., 1936) recomputed the elements in 1936 using all of the measured angles and his values are used here.

TABLE 4. *X*-RAY POWDER DATA. Fe RADIATION, Mn FILTER

Holdenite		*Mooreite*		*Torreyite*	
d	*I*	*d*	*I*	*d*	*I*
5.83	6	10.37	10	13.06	10
4.69	2	8.29	9	8.17	4
4.15	1	7.66	1	7.20	3
3.93	1	6.66	3	6.18	7
3.76	1	6.22	3	5.35	9
3.61	9	5.98	4	4.71	6
3.43	2	5.14	10	4.54	6
3.31	1	4.61	5	4.13	2
3.14	1	4.38	7	3.85	8
2.99	10	4.14	5	3.72	4
2.72	1	3.82	6	3.47	5
2.60	2	3.45	7	3.29	5
2.47	8	3.41	1	3.13	5
2.38	4	3.32	3	2.91	5
2.34	2	3.16	6	2.81	3
2.25	1	3.02	1	2.76	7
2.20	1	2.93	4	2.61	5
2.09	2	2.84	2	2.47	3
2.04	1	2.79	2	2.37	3
2.01	1	2.68	6	2.29	2
1.79	2	2.62	5	2.23	1
1.77	1	2.56	4	2.15	1
1.75	1	2.49	1	2.09	1
1.63	2	2.45	4	2.04	1
1.60	1	2.39	7	1.97	1
1.56	1	2.32	5	1.85	2
1.53	3	2.29	4	1.79	2
1.49	1	2.20	1	1.76	1
1.43	1	2.15	2	1.73	2
1.40	2	2.12	3	1.70	3
1.31	1	2.04	2	1.62	3
1.27	1	1.98	2	1.58	2
1.25	2	1.96	3	1.56	3
1.23	2	1.91	3	1.53	1
1.14	1	1.88	3	1.50	2
1.08	1	1.86	2	1.41	1
1.05	1	1.83	2		
1.04	1	1.79	3		
		1.76	1		
		1.74	7		

earlier than mooreite. The formula was given as $(Mg,Mn,Zn)_7(SO_4)(OH)_{12} \cdot 4H_2O$, with Mg:Mn:Zn = 5:3:4. It occurs only at Sterling Hill, N. J. No crystals have been found but an optical study indicated that it is monoclinic. There is a good {010} cleavage.

When a powder photograph of delta-mooreite was taken it was found to be quite different from that of mooreite. The powder data is given in Table 4 and the photographs are reproduced in Fig. 1. Thus, the two minerals are structurally unlike and are distinct species. A comparison of their properties is given in Table 3. A new name, *torreyite*, is proposed to replace the name delta-mooreite. Torreyite is in honor of John Torrey[4] (1796–1873), who was a natural scientist with special interests in botany, chemistry, and mineralogy. He received his early training in chemistry and mineralogy from Amos Eaton. Naming the mineral for him seems appropriate as he was one of the earliest workers at Franklin, publishing a paper on franklinite, willemite, and rhodonite in 1822.[5]

The material used for *x*-ray work was from the type specimen and was checked optically, by its specific gravity and spectrographically. The chemical analysis by Bauer follows:

MgO	17.27
MnO	17.98
ZnO	26.30
SO_3	11.64
H_2O	26.39
B_2O_3	present
SiO_2	0.08
	99.66

No mention of twinning was made by Berman but intricate polysynthetic twinning was observed in the present study. Using the universal stage the twin plane was identified as perpendicular to the {010} cleavage.

ACKNOWLEDGMENTS

The author wishes to express her thanks to Dr. Clifford Frondel, Dr. Charles Palache, Miss Mary Mrose, and Dr. Adolf Pabst for their assistance and advice.

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[4] Encyclopedia Britannica, 14th ed., 1929, vol. 22, p. 305. John Torrey: A biographical notice, *Am. Jour. Sci.*, 3rd series, **5**, 411–421.

[5] Torrey, John, *Am. Jour. Sci.*, Ser 1, **5**, 399–403 (1822).

QUARTZ SPHERE GROWN INTO A FACED CRYSTAL*

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and
Cornelius S. Hurlbut, Jr., *Harvard University.*

Abstract

A polished quartz sphere, subjected for 12 days to relatively high pressure and temperature in an alkaline solution with additional solid silica present, assumed through growth the morphology of a natural quartz crystal.

The crystal described below was grown from a polished quartz sphere used as a seed during an investigation† into the growing of synthetic quartz crystals by the Brush Development Company, Cleveland, Ohio. The crystal was grown in Run 25-3.

The polished sphere of optically clear quartz about 13.8 mm. in diameter was held near the top of a seven-inch deep autoclave by a silver wire. A quantity of quartzite fragments lay at the bottom under a solution of 3M sodium carbonate. The external temperatures were 376° C. at the top and 397° C. at the bottom, and the calculated pressure was about 700 atmospheres. During the period at the elevated temperature and pressure, the quartz at the bottom presumably dissolved slowly and formed a supersaturated solution in the cooler region at the top.

Similar development of a quartz sphere into a faced crystal was mentioned by Richard Nacken, one-time professor at the University of Frankfurt-am-Main, in a report on the "Synthesis of Oscillator Crystals" to the Nazi Government in 1944. This report was translated by the British Post Office Engineering Department and was made available by the U. S. Signal Corps. The translation is accompanied by a few figures, but those referring to the growth of the sphere are missing. The following is his description of the crystal:

"At points where the poles of the rhombohedral planes r $(10\bar{1}1)$ and z $(01\bar{1}1)$ of the quartz lie, bright and well-formed faces gradually extend. Along the crystallographic c-axis, growth was so rapid in both directions that a skeleton was formed. A basal plane was never observed; rhombohedral faces were always formed in the direction of this axis. Finally these also combine in a vertex bounded by the two rhombohedra, $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$. Toward the equator a number of contiguous rhombohedral faces are formed, which lend a barrel-like appearance to the crystal, with striations parallel to the equatorial plane. . . . Only after a much longer period of crystallization are prism faces also formed."

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* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 303.

† The investigation was carried out under contract with the U. S. Army Signal Corps.

Nacken's sphere was fed from vitreous silica, which he himself determined to be ten times as soluble as crystalline quartz, and increased in weight from 3.3 grams to 5.3 grams in four days.

Our sphere or, more correctly, spheroid, had the following dimensions: 13.48 mm. in the direction of the *c*-axis, 13.76 mm. in the direction of one of the *a* crystal axes, and 13.86 mm. along a direction at right angles to the other two. It increased about 39% in weight, from 3.6 grams to 5.0 grams, during the 12 days. No skeletal growth is shown and the prism faces are about as large as the rhombohedral faces. The latter seem to be of identical dimensions. Under a magnification of thirty-six diameters, several solution-vapor inclusions, are visible just below the surface of the rhombohedral faces.

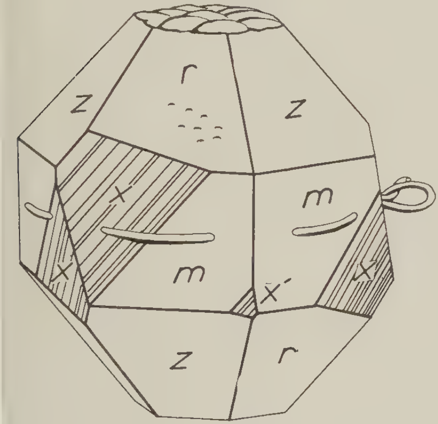

FIG. 1. Quartz crystal grown from sphere.

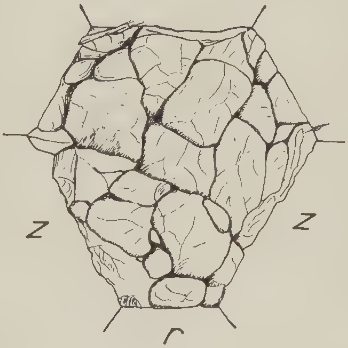

FIG. 2. Surface having the approximate position of the base.

The general appearance of the crystal strongly resembles a Herkimer County quartz crystal from which the apices have been broken (Fig. 1). The overall dimensions are 18 mm. (approximately) along the *c*-axis, 13.86 mm. between parallel prism faces, and 14.60 mm. between parallel rhombohedron faces. The distance between parallel prism faces is almost exactly the same as the equatorial diameter of the initial spheroid.

The forms displayed are the rhombohedrons $r\{10\bar{1}1\}$ and $z\{01\bar{1}1\}$, the prism, $m\{10\bar{1}0\}$, and the trigonal trapezohedron, $x\{51\bar{6}1\}$. The common form *s* is entirely lacking, but on two edges between *r* and *m* faces traces of the rhombohedron $\{20\bar{2}1\}$ are present. The rhombohedrons *r* and *z* are almost equally developed, giving the crystal a pyramidal aspect. Viewed along the extension of the *c*-axis, the nearly equal development of the rhombohedrons and of the six prism faces gives the outline of the crystal almost perfect hexagonal symmetry. The trigonal trapezohedral faces are, however, unequally developed, but their arrangement on the crystal shows it to be a left-hand individual. A single small trigonal trapezohedral face, x', in the twin position indicates twinning according to the Dauphiné law.

The rhombohedron faces display numerous minute imperfections, although they appear on casual inspection to be smooth and plane. Present on all the rhombohedron faces, but differing in size and number, are tiny protuberances. A few of these protuberances display microscopic terminal faces parallel to the rhombohedron upon which they occur, but in most cases they are rounded and featureless. In a few instances, the protuberance is the center of a system of concentric growth lines marking the boundaries of very shallow terraces. A few depressed areas of terrace growth can be seen under the binocular microscope which resemble a contour map of a theater-headed valley. Vicinal faces are common.

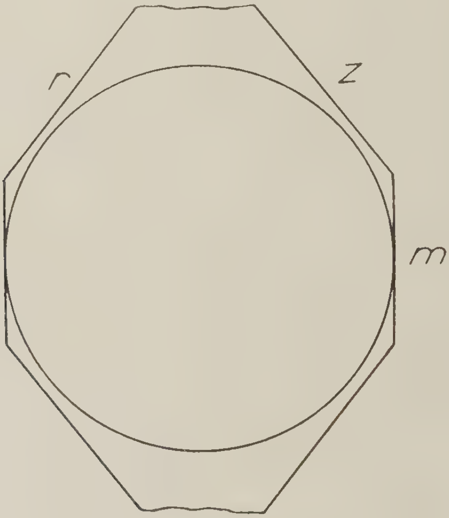

FIG. 3. Cross section of crystal and initial sphere.

The prism faces are essentially plane surfaces, free from the imperfections described above and lacking the usual horizontal striations. The x faces are deeply striated by oscillatory combination with the prism.

All edges and solid angles are sharp and show no skeletal growth, except at the ends of the c-axis. Here growth was incomplete and the rhombohedron faces terminate in a ragged, somewhat cracked and fissured edge bounding a pseudo-basal surface. This surface 4 to 5 mm. in diameter, although complex in detail (see Fig. 2), has in a gross way the position of the base. Examination on the optical goniometer reveals, however, that no trace of a reflecting surface parallel to {0001} exists. The surface is seen to consist instead of rudely rounded hummocks having in places a vague triangular shape parallel to one of the terminating rhombohedrons.

In order that the sphere could be suspended in the autoclave, it was notched at points around its equator so that a single loop of silver wire could hold it in place. New growth has completely filled in the notches, but a series of minute inclusions outline them in places. No such inclusions, however, mark the boundary between the initial spherical surface and the newly added quartz. Inasmuch as the silver wire emerges from the crystal at the center of each prism face, it is reasonable to assume that the prism faces are tangent to the initial sphere and that growth normal to them has been negligible. Moreover, the distance between the three pairs of prism faces is the same, 13.86 mm., equal to the diameter of the sphere.

A consideration of the dimensions of the crystal and of the initial sphere (Fig. 3) shows that growth took place most rapidly in the direction of the c-axis and was accomplished by addition of material to the rhombohedral faces. If the experiment had continued longer until the rhombohedral faces met at a point, further growth would undoubtedly have given rise to unequal development of the r and z forms.

Thanks are due to Dr. T. J. Turobinski who suggested the experiment and furnished the sphere, to Mr. Andrew R. Sobek who carried out the processing, and to Mr. Henry E. Wenden who aided in the crystal drawings.

NOTES AND NEWS

SOME NOTES ON THE POINT COUNTER

F. CHAYES, *Geophysical Laboratory, Washington, D. C.*

Several readers have written for further information about the point counter described in the January-February issue of this journal. I believe this information is sufficiently general to be worth publishing and I also wish to correct an error in the original article.

An exponent has been omitted from the right side of equation (1), page 5, which should read:

$$s_d^2 = \frac{1}{n} \overset{n}{\underset{i=1}{S}} (X_i - \mu)^2$$

The commonest query so far received concerns the possibility of buying the complete instrument; at the present writing this is not possible. A suitable mechanical stage may be purchased either from the American Optical Company (Catalogue No. 495), or from Bausch and Lomb (Catalogue No. 31–59–54). A five-cell counting block is provided by the Clay-Adams Company, New York, New York, and a six-unit block is offered by the Denominator Corporation, also of New York. Additional single cell counters may be obtained from the Veeder-Root Corporation, Hartford, Connecticut; three or four of these may be mounted on either of the multiple cell units.

Any reputable instrument shop can install click wheels on the mechanical stage. Macinco, Box 296, Kensington, Maryland, is prepared to make this installation on standard mechanical stages. On the projected Macinco model it will be possible to disengage the blades of the click wheels by a simple adjustment, so that the instrument can be used as an ordinary mechanical stage when not needed for quantitative work.

Unless the slide is firmly held in its clamp and the thrust collars and thread nut of the stage are well adjusted, the instrument does not come to rest properly at each click. At high speed this is usually not noticeable, but for fine-grained constituents which must be counted slowly it is bothersome. The thrust collars and slide clamp are easily adjusted by the operator, but adjustment of the thread nut is best left to a machinist. The original description was submitted for publication several months ago and the instrument has been in steady use since that time. To date more than 600 analyses have been run with it. Except for two settings of the thrust collars and the insertion of a shim in the thread nut, no adjustments have been necessary. Most of the counting has been done with a Clay-Adams 5-cell block on which two single-cell Veeder counters were mounted; this block is a pre-war model borrowed from the College Park Station of the Bureau of Mines, where it had been extensively used by myself and others. Except for a minor adjustment of the clearing bar, it has required no attention.

It is stated on page 1 of the original description that true Rosiwal analyses have not been made since introduction of the Shand micrometer in 1916, but this error is corrected in a hastily inserted footnote. The use of traverses so spaced that a single grain may be cut more than once does in fact violate a major condition specified by Rosiwal and places the procedure beyond the pale as far as the excellent study of Lincoln and Reitz (*Econ. Geol.*, 1913) is concerned. But this modification was suggested first by Wentworth, not by Shand. The use of evenly spaced traverses is now so ingrained that it has hardly been mentioned since it was first suggested by Wentworth in 1923, and in reviewing my typescript even such a meticulous critic as Dr. Shand himself failed to notice the error.

A NOTE ON THE CONVERSION OF AMORPHOUS SILICA TO QUARTZ

Donald A. Bailey, *The Saranac Laboratory, Saranac Lake, New York.*

In an earlier paper (1) it was pointed out that quartz or amorphous silica can be converted to cristobalite when heated for ten to thirty minutes with alkali fluxes at temperatures in the vicinity of 1150° C. A further investigation of several commercially prepared, finely divided amorphous silicas disclosed that crystallization of these substances could be brought about during ignition at temperatures between 1070° C. and 1100° C., provided CaO or $CaCO_3$ were present in amounts of five to ten per cent by weight. Before an opportunity to present the results had been realized, a paper on the crystallization of silicic acid by Schulman, *et al.* (2), appeared in a recent issue of the *American Mineralogist.* The authors show that quartz and cristobalite can form from silicic acid heated at 1150° C. for three hours in the presence of calcium, added as $CaCO_3$ or $CaSiO_3$. The present writer finds his results to be consistent with the observations of Schulman and his co-workers. Additional points revealed in the writer's investigation but not covered by Schulman's paper are discussed below.

In the experiments dealing with the conversion of silica to cristobalite (1), one sample in the series was a commercially prepared, finely divided amorphous silica. Following ignition of this sample at temperatures between 1070° C. and 1100° C., it was noted that over one-half of the substance was converted to quartz. The original material consisted of fine aggregates and sub-microscopic particles, and contained approximately five per cent calcium carbonate, the latter ranging in particle size from thirty microns to less than one micron. An x-ray powder photograph of the material prior to ignition showed no crystalline component aside from the calcium carbonate, and yielded a diffuse ring similar to that observed in x-ray diffraction patterns of vitreous silica (3). This diffuse ring was found to be in the position which it occupies in patterns of hydrated silica, such as opal and silica gel.

The discovery that quartz had been formed by igniting a sample of sub-microscopic amorphous silica that contained lime was an unexpected finding which called for further study. Ignition of this finely divided silica had been carried out by heating for thirty minutes a 200-milligram sample in a covered platinum crucible supported over a Meker burner. The substance lost approximately 11 per cent by weight and showed a marked shrinkage in volume. Microscopic examination between crossed nicols revealed that all of the calcite had been decomposed. The bulk of the material now had the appearance of cryptocrystalline quartz. Individual particles showed aggregate polarization and usually did not exceed twenty microns in size. The heated sample also contained fused masses having a refractive index near 1.63. This substance seems to be wollastonite. A powder photograph of the heated material+an internal standard showed a quartz pattern accounting for approximately 60 per cent of the sample. A faint line in the position of the principal wollastonite line and a very weak line indicating a trace of cristobalite were also apparent.

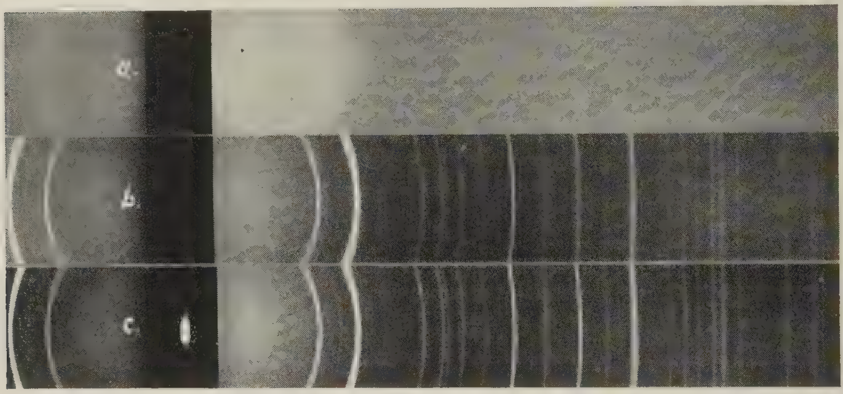

FIG. 1. *X*-ray powder diffraction patterns, Cu radiation, Ni filter. Samples held in wedge holder.

(a) Amorphous silica, containing 5 per cent calcium carbonate.
(b) Sample (a) after ignition at 1070° C. to 1100° C. for thirty minutes.
(c) Standard pattern for quartz.

A photograph without the internal standard shows a strong pattern for quartz (Fig. 1).

Following these observations on this one sample, a number of finely divided amorphous silicas were similarly heated for from five to thirty minutes after the addition of CaO or $CaCO_3$, or, in one case, $CaSiO_3$. Each sample, together with the flux employed, was moistened with alcohol and thoroughly mixed in a mullite mortar before and after the heat treatment. The materials chosen for the tests and the approximate percentages of crystalline silica formed, as determined by means of *x*-ray diffraction, are indicated in the Tables, 1 to 4. One test was included in which MgO was used. This material failed to bring about the conversion of amorphous silica to quartz. It is to be noted that the sample designated as "Silica No. 1" occurs in spherical particles ranging in diameter from 0.2 micron to less than 0.02 micron, as determined from electron micrographs. It contains 3.23 per cent CaO, 0.22 per cent MgO and 0.36 per cent alkalies (Na_2O+K_2O). The colloidal silica gel contains 0.18 per cent

TABLE 1

Silica No. 1 plus 10 Per Cent by Weight CaO
Ignited at 1070° C. to 1100° C.
Showing Effect of Time

Mixture after Ignition		Ignition time
Quartz per cent	*Cristobalite* per cent	minutes
n.f.	n.f.	0.5
15	n.f.	2
55	n.f.	5
55	trace	30

TABLE 2

Colloidal Silica Gel (contains 0.18% CaO)
Ignited Alone and with Fluxes at
1070° C. to 1100° C. for 30 minutes

Substance added		Mixture after Ignition	
		Quartz per cent	*Cristobalite* per cent
none		n.f.	n.f.
$CaCO_3$	10%	55	trace
CaO	10%	55	trace
$CaSiO_3$	10%	3	trace
MgO	10%	n.f.	n.f.

TABLE 3

Various Silicas Ignited with 10 Per Cent CaO at 1070° C. to 1150° C. for 30 Minutes

Silica	Mixture after Ignition	
	Quartz per cent	*Cristobalite* per cent
Silica No 1	55	trace
Colloidal Silica gel	55	trace
Vitreous Silica, 1–3μ	30	2
Diatomaceous Earth	17	30

TABLE 4

Vitreous Silica Ignited with 10 Per Cent CaO at 1070° C. to 1150° C. for 30 Minutes Showing Effect of Size

Vitreous Silica Size in microns	Mixture after Ignition	
	Quartz per cent	*Cristobalite* per cent
1–3	30	2
10–30	10	trace
75–200	2	trace

CaO. Samples of relatively coarse vitreous silica were also included among the tests.

An approximate estimate of the ignition temperature necessary to bring about conversion was made. Samples held at 820° C. and at 850 ° C. in a muffle furnace equipped with a pyrometer remained amorphous. Portions of these same samples when spread over the bottom of the platinum crucible to a depth of one millimeter and kept over the Meker flame for five minutes readily underwent conversion to quartz. The temperature on the inside bottom of the covered crucible was found to lie between the melting point of K_2SO_4 (1070° C.) and that of albite (1100° C.). The same burner was used in all of the tests, and efforts were made to maintain the gas and air supplies at constant levels.

RESULTS

It may be noted that where the grain size is sufficiently small, as in precipitated silicic acid and in samples of silica fume, conversion to quartz will take place in the presence of CaO within a few minutes, once the charge has reached the proper temperature (Table 1). These experiments do not exclude the possibility that some crystallization of the quartz may occur during the cooling of the samples and at temperatures somewhat lower than the maximum heat attained. CaO and $CaCO_3$ seem equally effective in bringing about conversion (Table 2). $CaSiO_3$ produced little quartz at the temperature employed, while MgO was inactive. Sosman (4) has suggested that liquid silicates, formed by the interaction of SiO_2 with certain oxides, including CaO, may act as fluxes, assisting in the sluggish inversions. It has been demonstrated that lime and silica when heated together at temperatures covering the range here explored will form calcium silicate (5). On the basis of the evidence, it seems probable that the true flux responsible for the conversions here noted is in every case a liquid silicate.

Anhydrous silica and silica gel yielded similar amounts of quartz when heated with CaO (Table 3). An increase in the grain size of vitreous silica retarded the rate of conversion to quartz (Table 4). In the diatomaceous earth sample, where small percentages of alkalies were present ($Na_2O+K_2O=0.7$ per cent), cristobalite was found to be in excess of quartz in the treated sample (Table 3).

ACKNOWLEDGMENT

The writer wishes to thank Mr. Thomas M. Durkan of the Saranac Laboratory for determining the lime content of two samples tested, and for advice regarding the preparation of this manuscript.

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AN IMPROVED METHOD OF ETCHING IRON METEORITES*

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AND
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There have been many descriptions of the technic by which the structural patterns of the different components in iron meteorites can be developed. The oldest method was by heating a thin section of the meteorite over a burner and a contrasting pattern would result because the various components oxidized differently. This method is seldom if ever used today. Liquid etching agents give better patterns and can be more easily controlled to bring out the desired degree of etching. Most of the iron meteorites in the past 25 years have been etched with dilute nitric acid. It was also recommended that any nodules of troilite, etc., should be lacquered before the application of the etching solution. This precaution is not necessary in the method for etching iron meteorites that is now employed at the U. S. National Museum, and the etched surface obtained by following the method here described gives a much more attractive surface than was obtainable from all the other etching methods tried in our laboratories.

Preparation of the surface to be etched

If a satisfactory macro-etch is to be obtained, the surface must be carefully prepared. It is important that the following preliminary steps be taken to properly prepare the surface. The surface of the meteorite to be etched is ground down with 100 mesh carborundum until it is perfectly flat. The grinding should be continued until the area is as smooth as it can be made with the 100 mesh carborundum.

The meteorite is then washed with water and brushed to completely remove the abrasive. This must be done thoroughly otherwise there is the possibility that some of this coarse material will free itself from some of the cracks in the meteorite and scratch the finish during the subsequent grinding and polishing operations. Between each of the three stages in the grinding of the surface this washing operation must be done with great care.

After the 100 mesh carborundum is removed, the grinding is continued using 320 mesh or FF carborundum until the surface is as smooth as this abrasive can make it. After washing, the slice of meteorite is ready for the third and final grinding with 600 mesh carborundum. This must be carried to a point where no scratches remain on the surface. It is desirable to examine the face with a low power magnifying glass to make certain that it is smooth.

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Occasionally this process must be carried one step further, and that is to polish it with tin oxide on a felt buffer. The surface of the meteorite after the final grinding with 600 mesh carborundum, or the polishing operation, if it was necessary, is now ready for etching provided it is perfectly clean and free from all scratches.

Preparation of the etching solution

This solution should be freshly prepared for each application and with a little experience the operator will soon learn to estimate the quantity needed.[1] Concentrated nitric acid is mixed with grain alcohol in the following proportions: 2 parts of nitric acid and 5 parts of alcohol. To this solution some carpenter's glue is added by permitting about one drop of the glue to fall upon a glass stirring rod near the end of the rod and then plunging the rod into the solution and stirring immediately.

A swab is prepared by attaching a clean piece of soft white cloth to the end of a glass stirring rod, in such a fashion that about 1 inch of the cloth overhangs the end of the rod making a wide swab.

Etching procedure

The etching is then most conveniently done at a sink where water is available for immediate removal of the etchant after the desired etching effect is attained. Place the iron on a board so the surface to be etched is flat. Then pour the etchant on the meteorite so that the entire surface is quickly covered with the solution and start at once to scrub the etching solution over the entire surface with the swab. The entire area should receive equal amounts of the etchant and also get about the same degree of scrubbing. It is important for the operator to move the swab rapidly over the complete surface to prevent any excessive accumulation of the acid in any one spot. Some of the etchant may run down the side of the meteorite, but this has no serious effects as the outside usually is coated with an oxide film that will retard any appreciable chemical action. The swabbing is continued without interruption until the proper structure has been developed, or until the operator sees that the corrosive action of the etchant has stopped. Usually it is necessary to apply a second and sometimes a third application of the etchant.

Meteorites vary considerably in their reaction to the etching solution. Some etch much slower than others so it is not possible to predict the time required to produce the desired effect. Rarely is it possible to etch a surface in less than 15 minutes and sometimes 45 minutes will be needed.

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[1] A surface with an area of 10 sq. inches will require 5 ml. HNO_3 (conc.) and 12 ml. of grain alcohol. To this mixture add one drop of carpenter's glue.

When the operator thinks that the etching is deep enough, the etchant is washed off with alcohol and the application of alcohol repeated a second time. This washing is followed by two or three minutes of washing in a stream of running water with continued brushing. The etched face is then rewashed with alcohol at least twice to remove the water, and then dried before an electric fan.

It occasionally happens that a spot will appear which has a slight tarnish. Sometimes this can be effectively removed with a clean rubber eraser, but if the spot does not yield to light rubbing it will be necessary to reetch the meteorite with a freshly prepared etching solution made up to contain one half the quantity of nitric acid used in the first solution.

This method gives an etched surface on a meteorite which is more lustrous than can be obtained by using nitric acid or nital (5% nitric acid and alcohol). If the meteorite is free from lawrencite, the etched surface will remain bright and in perfect condition as long as it is not touched with the fingers. This surface does not require protection of lacquers. Prior to the development of this method by Mr. B. O. Reberholt, the meteorites in the display cases in this Museum required refinishing every year or so. The present display of iron meteorites was installed nearly 8 years ago and none have required any refinishing.

BODENBENDERITE, A DISCREDITED SPECIES*

Charles Milton and Alfred Tennyson Myers,
U. S. Geological Survey, Washington, D. C.

In 1928 Eberhard Rimann (1) proposed the name bodenbenderite for a supposed new compound of composition given as $(Mn,Ca,Fe,Mg)_4Al[(Al,Y)O][(Si,Ti,U)O_4]_3$. The proposed new species was received with some reserve; thus, J. F. Schairer (2) in 1929 commented that the data were unsatisfactory; in 1932 Dana-Ford (3) listed bodenbenderite in small capitals, signifying a species of doubtful validity; in 1934 Larsen-Berman (4) suggested a possible relationship to beckelite, notwithstanding considerable differences in the formulas ascribed to the two substances. In 1941 Strunz (5) listed it, as probably a variety of garnet, with a question mark as denoting an inadequately defined "mineral."

Recently, Dr. Michael Fleischer of the Geological Survey brought to our attention the unsatisfactory status of bodenbenderite. Through the kindness of Dr. William F. Foshag, of the United States National Museum, a specimen of the original material (U.S.N.M. 95804) was made available for study. This had been obtained from Rimann shortly after his two papers were published.

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The two papers by Rimann, one in German, the other a Spanish translation, to which latter is added a spectrographic study, give in much detail the chemical analytical work, from which the composition of the supposed mineral was determined. However, a casual glance at a thin section of the material would have shown the hopelessness of interpreting even a good analysis of such a mixture. The microphotograph (Fig. 1) shows the complex intergrowth of the material.

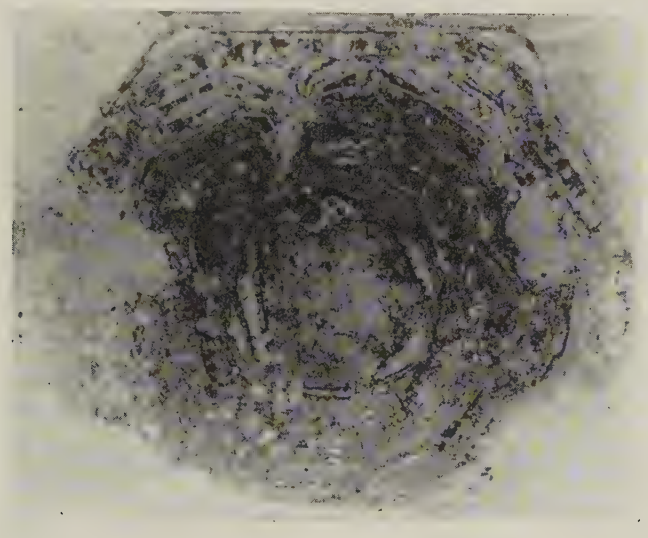

FIG. 1. "Bodenbenderite" = spessartite, fluorite, etc.
× 9 thin section. The opaque layers may be mixtures of spessartite with manganese oxide; the spessartite forms thin shells interlayered with much fluorite, chlorite, albitic plagioclase, etc.

Carefully selected crushed fragments of the cleanest possible material gave good *x*-ray patterns, which our co-worker Joseph Axelrod found to consist solely of the lines of garnet and fluorite. Spectrographic study gave the following data, which are presented along with Rimann's analysis (by E. Gruner).

The major discrepancies are in TiO_2, CaO, and Y_2O_3 (yttria earths).

The analysis by Gruner is that of "selected as pure as possible material" with "admixture of fluorspar, penninite, and CO_2 (sic)." Furthermore, the percentages given are an average of two analyses, with no data listed as to their divergence. It is supplemented by two others, both also the average of two analyses. One is that of the portion dissolved in eight

	A. T. Myers (spectrographic)	E. Gruner
SiO_2	XO.	20.2
TiO_2	.X	7.4
MnO	XO.	34.3
FeO	X.O (Total Fe)	.3
CaO	XO.	5.5
MgO	.X	.3
Al_2O_3	XO.	10.7
Fe_2O_3		1.2
Y_2O_3	.OX	13.2
Er_2O_3		
K_2O		.2
Na_2O		.3
H_2O		1.3
CO_2		3.8
U_3O_8		.4
F		2.3

hours in hot $4n$ HCl; the other, that of the insoluble residue. After deductions for CaF_2, gaseous (!) CO_2, muscovite, hematite, and moisture, totalling 16.7 per cent of the first analysis, the residue is computed to the formula ascribed to bodenbenderite.

It is hardly worth while to discuss in detail the methods of an obviously bad analysis; however, it seems likely that the major errors were (1) failure to remove fluorine completely, evaporation of the sodium-carbonate melt with HCl at 110° C. being insufficient, and, as is well known, fluorine affects adversely the determination of many if not most elements; (2) it is likely that Gruner precipitated calcium or manganese, or both, as oxalates, mistaking the precipitate for rare-earth oxalates. The oxides weighed as yttrium earths were therefore in all likelihood calcium, probably with some manganese.

It may be noted here that spessartite garnets do carry small but detectable quantities, usually on the order of hundredths of a per cent, of yttrium earths. An investigation of this by Howard Jaffe and Charles Milton is in progress and will appear in this journal.

In the spectrographic discussion forming part of his paper in Spanish, Rimann mentions that in the visible spectrum, in order of intensity, there were recognized: Ca, Mn, Al, Mg, Na, K, Si, Fe, Ti, Y, Er, Nd, Pr, which is not the order of abundance given by his analysis with respect to Mg, Na, K, Ti, and the rare earths, but does agree with our spectrographic data in the ultra-violet.

In summary, the name bodenbenderite for a mineral species has no justification and should be dropped.

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CORRECTIONS TO RECENT PAPERS ON PROBERTITE AND LINDGRENITE

WILLIAM H. BARNES, *National Research Council, Ottawa, Ontario.*

In a recent paper on "The Unit Cell and Space Group of Probertite" (*Am. Mineral.*, **34**, 19–25 (1949)), at the bottom of p. 23 and the top of p. 24, Ft_c^* and Ft_a^* are shown equal to Fd_c^* and Fd_a^*, respectively. Since probertite is monoclinic, this is, of course, not true (see bottom of p. 22) when t^* and d^* have their usual significance. The manuscript of this paper was completed in March 1948 and, at the present date, I am unable to offer any explanation for this error except the possibility of an automatic but irrational reflex in making the *b Axis, Zero Level* data symmetrical in appearance with those for the *a Axis, Zero Level.* The aberration does not appear in my original notes. At the bottom of p. 23, *c^* translation (t_c^*) and spacing (d_c^*)* should read *c^* spacing (d_c^*)* and, at the top of columns 2 and 4, $Ft_c^*=$ should be deleted. Similarly, at the top of p. 24, *a^* translation (t_a^*) and spacing (d_a^*)* should read *a^* spacing (d_a^*)* and, at the top of columns 2 and 4, $Ft_a^*=$ should be deleted.

For the data presented in "The Unit Cell and Space Group of Lindgrenite" (*Am. Mineral.*, **34**, 163–172 (1949)), photographs obtained with copper radiation were used. Subsequently other crystals were examined with molybdenum radiation. Since diffraction photographs of the latter, of course, show many more reciprocal lattice points, they were selected for reproduction. Due to the small difference between d_c^* and d_a^* the identities of the c^* and a^* axes have been assigned incorrectly in Figs. 7, 8, 9, 10, pp. 168, 169. Thus under Figs. 7 and 8, *new a axis* should read *new c axis* and under Figs. 7, 8, 9, 10, (*new c^* horizontal*) should read (*new a^* horizontal*). In this connection measurement of the original negatives of Figs. 7 and 9 to check this point has given values for c^* and a^* within 0.3% of those obtained previously using a different crystal, a different radiation and a different Buerger precession film measuring device, thus further illustrating the good reproducibility of results obtained with the precession camera.

I am indebted to Professor D. Jerome Fisher for drawing my attention to the slips herein corrected.

An International Committee for the Study of Clays (Comite International pour l'Etude des Argeles, CIPEA) was organized in London in August, 1948, at the time of the meeting of the International Geological Congress. S. Henin of France was elected chairman, and M. Lepingle of Belgium secretary. The Committee is limited to not more than two representatives from each country. The members of the Committee from the United States are R. E. Grim of the Illinois State Geological Survey and W. P. Kelley of the University of California.

The Committee is to function through an executive sub-committee which was designated at the meeting in London as follows:

S. Henin, France
M. Lepingle, Belgium
R. E. Grim, U. S. A.
D. M. C. MacEwan, Great Britain

The Committee wishes to include all phases of clay research and workers on clay in all specialized fields. Its objects are to bring together a complete documentation on the studies of clays and their means of study, to facilitate contacts between specialists in these studies and to hold periodic meetings in the course of which all questions relative to clays will be examined and discussed.

In order that all the specialists can most easily compare their results and that they may speak in effect "the same language," it will facilitate the exchange of reference samples among research workers and will make every effort to make more precise the terminology used in the science of clays as well as the methods used.

It is planned that the members of the International Committee will effect liaison between the International Committee and the research workers of each of their countries. In some countries national committees are being organized with their officers acting as members of the International Committee, for example in Belgium, France, Great Britain, and Sweden.

Questionnaires on the subject of the various questions raised by the International Committee will be sent to the members from each country who will be responsible for distributing them in various countries and obtaining replies.

The first activity of the Committee concerns standardization of the differential thermal procedure, and a statement concerning plans for studying the problems is being prepared.

Cenogonal, a new crystallographic term has been suggested by Professor A. F. Rogers to designate angles that are common to two or more crystal species. Cenogonal angles include the angles in the tetragonal zone [001] of the tetragonal system as well as the angles in the hexagonal zone [00-1] of the hexagonal system and all the angles between the faces of crystals in any one of the zones of the isometric system. (*Science*, Dec. 17, 1948, vol. **108**, No. 2815, pages 692–693.)

The New York *Times* reported the death of Frank J. Keeley on April 12, at the age of 81 years. Mr. Keeley was curator of the William S. Vaux mineral collection at the Academy of Natural Sciences at Philadelphia. A Fellow of the Royal Microscopical Society of London, he developed methods for the use of microspectroscopy in identifying precious stones.

The Geology Department of the School of Mines and Metallurgy, University of Missouri, Rolla, Missouri, would like to announce through *The American Mineralogist* the availability of teaching assistantships and fellowships in the fields of mineralogy and economic geology for the school year, 1949–1950.

Applications may be made either to the Chairman of the Department of Geology and Mineralogy or to the Chairman of the Committee on Graduate Study.

Methyl-ethyl ketone as an index liquid. In published lists of liquids for determining refractive index, acetone is often included, but the advantages of the related methyl-ethyl ketone are usually overlooked. The latter compound, which is now marketed by many chemical manufacturers, is less volatile than acetone, and also has a more agreeable odor. Its refractive index is about 1.375. This happens to match the alpha of magnesium oxalate, so the ketone itself may be used as immersion liquid to distinguish this salt from calcium oxalate, both of these occurring in plant tissues. (Wherry and Keenan, *Jour. Am. Pharmaceutical Assn.*, **12**, 301, 1923.)

(EDGAR T. WHERRY, University of Pennsylvania.)

Sydney Ball, mining geologist and consulting mineralogist to the U. S. Bureau of Mines, died in New York City on April 8, at the age of 71 years.

The twelfth annual meeting of the Meteoritical Society will be held Sept. 6 and 7, 1949, at the University of Southern California, Los Angeles, California. Titles and abstracts of papers to be presented should be sent to John A. Russell, Dept. of Astronomy, University of Southern California, Los Angeles 7, California.

PROCEEDINGS OF SOCIETIES

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held Thursday, March 31, 1949, in the apartments of the Geological Society of London, Burlington House, Piccadilly, W. 1 (by kind permission).

The following papers were presented:

(1) The Petrology of the Evaporites of the Eskdale No. 2 Boring, East Yorkshire. Part 1.—The Lower Evaporite Bed.

By Dr. F. H. Stewart

A study has been made of rocks from the lowest of the three Permian evaporite beds passed through by the D'Arcy Exploration Company's boring in 1938–39, near Aislaby, Eskdale. The bed is 460 feet thick and is underlain by dolomite. It can be divided into four main zones:—

Halite-anhydrite zone, with predominant halite (86 feet).
Upper anhydrite zone, with subordinate halite and carbonate (41 feet).
Polyhalite zone, with subordinate anhydrite, and a halite-rich upper part (85 feet).
Lower anhydrite zone, with subordinate halite and carbonate (248 feet).

Many of the rocks have suffered large scale changes due to replacement and recrystallization since their original precipitation. Polyhalite is believed to be a secondary mineral and has replaced anhydrite and halite. Many other replacements are noted. Most of these changes were probably due to the action of percolating brines during the formation of the evaporite bed.

Other points discussed are the occurrence of early gypsum in the polyhalite zone, the distribution of dolomite and magnesite, and the occurrence of talc.

(2) A New Barium Mineral from the Benallt Manganese Mine, Rhiw, Carnarvonshire

By Dr. W. Campbell Smith, Dr. F. A. Bannister and Dr. M. H. Hey

Small, white prisms and thin, colourless plates R.I. ϵ 1.612, ω 1.622, uniaxial $-$, sp.gr. 3.41, found on manganese ore prove to be a new hydrated barium aluminium silicate. Microanalysis and x-ray study show that the hexagonal rhomb-based unit cell, $a=5.32$, $c=7.67$ Å contains $BaAlSi_3O_8(OH)$.

(3) Plagioclases from Sultan Hamud, Kenya

By Mr. P. M. Game

Analyses have been made and empirical unit cell contents calculated for an albite-oligoclase and an oligoclase from Sultan Hamud, Kenya. Most of the determined optical properties are in good agreement with the corresponding values measured by previous workers; the R.I.'s are, however, lower by about .001 than the mean of selected previous determinations. The poles of (001) and (010) fall close to the appropriate Reinhard migration curves, but indicate an anorthite content from 3 to 4% lower than that derived from the analyses.

(4) Some Problems on Determining Optical Constants and the Thickness of Thin Sections

By Mr. P. M. Game

Plagioclases from Sultan Hamud, Kenya, have been used for these investigations. Parallel plates of different orientations were rotated on a refractometer and curves were drawn to show the resulting movement of the shadow edges. The values of α and γ are immediately obtained from these curves, but the ambiguity in the determination of β has long been recognized. A practical trial of the most recently suggested method of distinction, that of E. J. Burbage and B. W. Anderson, casts some doubt on the validity of the formula proposed and shows its restricted use. It is concluded that the most accurate value of β is that found by calculation from the measured values of α, γ and 2V. The reliability of 2V as obtained by direct measurement is compared with the results derived by calculation from birefringence values, small errors in which cause relatively large errors in the optic axial angle calculated from them. Investigation of the errors involved in microscopical determinations of thickness shows a persistent tendency to over-estimate; better results may be expected by focussing on cleavage cracks rather than on dust particles.

(5) Silica Percentage as a Factor in Rock Classification

By Dr. A. K. Wells

By plotting total silica against free silica (quartz) in the igneous rocks, it is shown that it is impossible to separate granites and granodiorites from syenites and diorites on a silica-percentage basis. The causes of the variation in mineral content of rocks of the same SiO_2-percentage are examined.

(6) Unusual Dolomite from Portsoy, Banff

By Mr. W. T. Harry and Mr. E. M. Patterson

Serpentine near Portsoy, Banff, occasionally bears irregular dolomite masses of most unusual appearance. These measure up to 1 inch across, resemble white calcite and present large flat cleavage surfaces. Each is a single crystal, interpreted as a large porphyroblast developed during retrogressive metamorphism through replacement of serpentine by CaO- and CO_2-bearing solutions. Two chemical analyses of the mineral demonstrate a noteworthy absence of iron and a high barium content.

(*Titles and abstracts submitted by G. F. Claringbull, General Secretary*)

BOOK REVIEWS

DANA'S *MINERALS AND HOW TO STUDY THEM*. Third Edition by CORNELIUS S. HURLBUT, JR.

With the publication of the completely revised and largely rewritten third edition of Dana's *Minerals and How to Study Them* by Cornelius S. Hurlbut, Jr., three of the four "Dana family" mineralogical books now have been completed or partly completed in modern versions. Volume I of the Dana *System of Mineralogy*, 7th edition, by Charles Palache, the late Harry Berman, and Clifford Frondel has partly fulfilled the long felt need for a complete compilation of mineralogical data. It is to be hoped that volume II of this encyclopedic work will not be inordinately delayed. Dana's *Manual of Mineralogy*, 15th edition, also revised by Professor Hurlbut, has shown itself to be an excellent textbook for students of elementary mineralogy. *Minerals and How to Study Them* is a sound initial rung on the ladder leading to mineralogical training and experience; it is advertised as "A book for beginners in mineralogy." It is to be regretted that there has appeared no modern counterpart of Dana's *A Textbook of Mineralogy*, the 4th and last edition of which was revised by the late Professor Ford in 1932. This volume, on an advanced mineralogical level, is now outdated, but deserves the renovating treatment accorded the other three "Danas."

Minerals and How to Study Them contains the original eight subdivisions of the first edition of 1895. Their titles have been slightly modified and their contents have been completely transformed on the basis of modern mineralogy. The introductory statement, "Minerals and Mineralogy," is followed by a short chapter outlining the fundamentals of mineral collecting and study. A long section on "Crystals and Crystal Habits" broaches the nature of crystals, the crystalline state, and crystal symmetry. Included here are descriptions of the six crystal systems and their principal forms. Other topics treated under this heading include the simple measurement of crystal angles, crystal irregularities, crystal aggregations, and an interesting and valuable summary on growing artificial crystals.

Chapter four describes the physical properties of minerals and chapter five their chemical properties. Blowpipe and elementary chemical methods of identification are next discussed, but, as the preface indicates, this chapter has been considerably shortened. Its contents and organization are adequate in view of the declining emphasis afforded these determinative devices. Descriptions of individual minerals appear in chapter seven. About 150 species are described in some detail and many others are mentioned. Individual descriptions follow the standard headings: habit, physical properties, composition, and occurrence. The selection of only 150 representative species is, of course, a very difficult task, and the choices of the older editions have been retained in large part. Some omissions, however, are notable, as for example, aegirine and columbite. Surely these are more important to the beginning student and are more likely to be encountered by the apprentice collector than are native antimony and native arsenic. Although the terms limonite and bauxite have been retained, the analogous name wad, a useful designation for mixtures of manganese oxides unidentifiable by elementary means, is not mentioned. As usual a description of ice as a mineral is included. The arrangement of the species follows that of the new "Dana System," in a general way and is described as a chemical classification. Quartz, however, is placed at the head of the silicate group, so that the classification is in part, at least, chemical-structural.

The book concludes with a section on mineral determination and a group of very valuable determinative tables based initially on luster and subdivided first on hardness, then on cleavage. Appendix I contains a list of common minerals grouped under their most important elements and Appendix II lists the most important minerals for a small collection. The index is complete and useful. The volume contains 323 pages and 387 figures.

The crystal drawings are uniformly excellent, as are many of the other line drawings and engravings, some of which have been retained from the first edition. Several sketches of minerals by Lougee are outstanding, and two handsome color plates grace the frontispiece. The other photographs show a considerable range in quality. Most are adequate to very good but a few fail to reveal significant mineralogical features or are lackluster, for example, that of heulandite (Fig. 332), asbestos (Fig. 338), and hemimorphite (Fig. 363).

The book is well printed; the paper is excellent; and typographical errors appear to be at a minimum. Professor Hurlbut's careful and competent revision has undoubtedly produced a high quality book that will be of unusual interest and of outstanding value to the mineralogical novice, either amateur or future professional. *Minerals and How to Study Them* is published by John Wiley & Sons, Inc. and is priced at $3.90.

E. Wm. Heinrich

GESCHICHTE DES GOLDES, by Heinrich Quiring.

Professor Heinrich Quiring, Director of the Geological and Mineralogical Institute of the Technical University of Berlin, has compiled an interesting and detailed account of the "History of Gold." The paper bound volume of 318 pages is published by the Ferdinand Enke Verlag of Stuttgart and is priced at 34 German marks. In the introduction the work attempts to relate the development of cultures to their gold supply. In the author's opinion, an ample supply of gold has hastened the development of certain civilizations and has stimulated their growth; whereas inadequate or meager quantities of the golden metal accompany a declining culture or act as drags on its formation. This brief theoretical argument attempts but inadequately, it seems, to answer the well known query, "Which came first—the hen or the egg?" Certainly vigorous civilizations sought an ample gold supply which in turn was used to promote further expansion. As the author opportunely quotes, "Hunger *nach* Gold endeckte die Welt" (italics the reviewer's).

The following four sections trace the history of gold through the Bronze Age, the Iron Age and the Roman emperor period, the Middle Ages, and the Modern Age (since 1493). Each period is subdivided on a geographical basis. The book is a veritable encyclopedia of "golden" facts, and anyone interested in history, archaeology, gold mining, or historical mineralogy will profit by reading it. From random pannings we glean such diversified colors as: the Egyptian king Tutanchamon (1357–1351 B.C.) was buried in a casket of gold weighing 110 kg.; rings used in Bremen, Germany, in the late bronze age were made of Irish gold; in late Babylonian times the ratio value of gold to silver was from 8.5:1 to 14:1; the first important discovery of gold tellurides was at Nagyág, Hungary; in 1758 the export of platinum from Colombia was forbidden because it was used to adulterate gold coinage; and in 1941 Colorado produced 11,700 kg. of gold, only 5% of which came from placer deposits.

E. Wm. Heinrich

Part II of *Die Entwicklung der Chemischen Elemente* by N. Efremov has been published recently in German by Ihor Belej of Munich 17, Germany. A second edition of Part I of the same work, which was reviewed in *The American Mineralogist*, **32**, 699–700, 1947, also has been issued. Part II contains "sketches on geochemistry from the viewpoint of transformation in atomic nuclei," and touches on such matters as mineral paragenesis, age relations among various rock types, explosion pipes, desilicated pegmatites, origin of gabbro-anorthosite-charnockite complexes, and quartz-carbonate rocks in serpentine. Like its predecessor, it is a theoretical attempt to explain mineral transformations in terms of atomic transmutations rather than as chemical (i.e., extranuclear) reactions.

The American Petroleum Institute of Dallas, Texas, has published Preliminary Report No. 1, *Glossary of Clay Mineral Names* by Paul F. Kerr and P. K. Hamilton of Columbia University. This useful compilation gives definitions, brief descriptions, histories, and main references to 246 minerals and mineral substances belonging to the clay group and to closely allied groups.

E. Wm. Heinrich
University of Michigan

NEW MINERAL NAMES

Koktaite

Josef Sekanina, Koktaite, a new mineral of the syngenite group: *Acta Acad. Sci. Nat. Moravo-Silesiacae* **20**, No. 1, 26 pp. (1948) (Czech with French summary); through *Mineralog. Abs.*, **10**, 352 (1948). Pseudomorphs after gypsum were found, associated with gypsum, mascagnite, and ammonium alum in a lignite mine at Zeravice near Kyjov, southeast Moravia. *X*-ray photographs are similar to that of syngenite. The optical data agree with those determined on artificial ammonium syngenite, $(NH_4)_2Ca(SO_4)_2\cdot H_2O$. The crystals are monoclinic, acicular, with the forms: $\{100\}$, $\{110\}$, $\{001\}$, $\{011\}$, and $\{101\}$, no cleavage, twins on $\{100\}$ frequent. Optically biaxial, neg., $\alpha=1.524$, $\beta=1.532$, $\gamma=1.536$, 2V 72°. Sp. gr. 2.09. Decomposed by water with precipitation of gypsum. Origin of name is not stated in abstract; perhaps named for J. Kokta, who analyzed the artificial salt.

Michael Fleischer

Dervillite

R. Weil, La dervillite, espece minerale nouvelle:

Rev. sci. nat. Auvergne, Clermont-Ferrand, **7**, 110–111 (1941); through *Mineralog. Abs.*, **10**, 353–354 (1948).

"Small (0.3 mm.) crystals found in a cavity in native arsenic from Gabe Gottes mine, Sainte-Marie-aux-Mines, Haute-Rhin (=Markirch, Alsace) are brownish-black with metallic luster, black streak, low hardness, very brittle, and show at least one direction of cleavage. They are soluble in HNO_3 ,and contain Sb, Pb, perhaps also Bi, and little sulfur. A crystal measured by H. Ungemach, monoclinic, $a:b:c=1.0691:1:1.4853$, with 8 forms, has been lost, and no more material has been found. The *x*-ray powder pattern is distinct from that of lautite and other minerals from the locality."

Discussion: It is regrettable that the literature should be burdened with a name for such incompletely described material.

M. F.

Varlamoffite

H. Buttgenbach, Les mineraux de Belgique et du Congo Belge 1947, pp. 182–183; from unpublished work by DeDycker.

Name given to a yellow, earthy, porous mass of density 2.52 to 2.61 and supposedly H_2SnO_3. The average of three analyses by Mlle. Gastellrei gave H_2SnO_3 59.22, SnO_2 25.55, SiC_2 1.68, Fe_2O_3 9.45, Al_2O_3 2.22, H_2O 2.12; sum 100.24%. Occurs in tin-bearing veins of Kalima and other regions of Mamiema, Belgian Congo.

Discussion: Compare the similar souxite (*Am. Mineral.*, **32**, 372, 1947).

M. F.

Phosphoscorodite

T. N. Shadlun and Y. S. Nesterova, Phosphoscorodite from Blyav (southern Urals): *Zapiski Vserossii Mineral. Obshchestva* (Mem. soc. russe mineral.), **76,** 212–215 (1947); through *Chemical Abstracts*, **43,** 2898 (1949).

Analysis of finely crystalline white material in the oxidation zone of the pyrite deposits of Blyav gave: As_2O_5 26.12, P_2O_5 16.03, SO_3 1.82, Fe_2O_3 40.32, H_2O 16.46%. G. = 3.35–3.5; $\alpha = 1.758$–1.762, $\gamma = 1.777$–1.789; biaxial, positive.

Discussion: The composition, as given in the analysis above, corresponds to 50.2% scorodite, 49.8% strengite, but the optical data indicate a composition closer to that of scorodite. The new name is unnecessary; phosphatian scorodite should be used.

M. F.

Paraguanjuatite

Paul Ramdohr, Las especes mineralogicas guanajuatita y paraguanajuatita: *Comite Direct. Invest. Recursos Minerales Mexico Bol.* **20,** 1–15 (1948).

A portion of some specimens of guanajuatite, $Bi_2(Se, S)_3$, from the type locality, the Santa Catarina Mine, Guanajuato, Mexico, were found to be rhombohedral paramorphs after the original orthorhombic mineral. The rhombohedral mineral, named paraguanajuatite, corresponds to Bi_2Se_3 synthesized by Carpanese, *Periodico Mineral.* (Roma) **8,** 289–290 (1937). Optical and x-ray data are given. From powder photographs, $a_0 = 4.076$ Å $c_0 = 54.7$ Å. The structure is similar to those of tetradymite and tellurobismuthite.

M. F.

NATIONAL RESEARCH COUNCIL NEWS RELEASE

Appointment of Dr. David M. Delo of Washington, D. C., as the first Executive Director of the American Geological Institute, was announced today (June 3, 1949) by Dr. Detlev W. Bronk, Chairman of the National Research Council.

The American Geological Institute is a new organization established in November 1948 which will represent the profession of geology. It is composed of a union of eleven geological societies whose members total more than 10,000 professional geologists. Headquarters will be located in the National Research Council, 2101 Constitution Ave., Washington 25, D. C., and the activities of the Institute will be carried on in conjunction with those of the Division of Geology and Geography, NRC.

The primary objectives of the new Institute are the advancement of geology and its application to human welfare by providing a means for the cooperation of organizations active in the fields of pure and applied geology. Membership is open to all non-profit organizations concerned with the earth sciences—geology, geophysics, geochemistry, mineralogy, etc. The initial member organizations are:

American Association of Petroleum Geologists
American Geophysical Union
American Institute of Mining and Metallurgical Engineers
Geological Society of America
Mineralogical Society of America
Paleontological Society
Seismological Society of America
Society of Economic Geologists
Society of Economic Paleontologists and Mineralogists
Society of Exploration Geophysicists
Society of Vertebrate Paleontology

The Institute is organized as an instrument of the National Research Council, in this way uniting geologists with all other American scientists who are seeking solutions to problems which can be attacked best through group or united action. Initially its functions will be concerned primarily with the non-research activities of the Geological profession, and will supplement the work of the Division of Geology and Geography of the National Research Council which is chiefly concerned with the coordination of research in geology and geography and its interrelationships with allied sciences.

Officers of the Institute are A. I. Levorsen, Dean of Mineral Sciences, Stanford University, president; W. B. Heroy, Beers and Heroy, Dallas, Texas, vice-president; and Earl Ingerson, U. S. Geological Survey, Washington, D. C., secretary-treasurer.

Dr. Delo began his duties on 1 June. He has served for the past three years as Chief of Scientific Manpower for the Research and Development Group, Logistics Division, General Staff, U. S. Army. During the World War II he was a Technical Aide in the Office of Scientific Research and Development and prior to that time was Chairman of the Department of Geology and Geography, Knox College.

The new Executive Director is a graduate of Miami University (Ohio) and received his doctorate degree from Harvard Univerity. He is a Fellow of the Geological Society of America and a member of Phi Beta Kappa and Sigma Xi.

TWO NEW MINERALIGHTS

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Now, the new MINERALIGHT model L ultra-violet lamp makes filtered long wave ultra-violet available to all laboratories, small and large alike, at a very low price. The new model L MINERALIGHT is a compact, light weight device that transforms electrical energy into ultra-violet light of largely 3660 Angstrom Units wave length, widely favored because of its versatility in fluorescence analysis. The lamp operates on 110 volt A. C., 50-60 cycle current and comes complete with transformer and cord, ready to operate. The transformer has a switch for on-off control.

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(* Shipment of uraninite must be made by express since radioactive minerals are prohibited from the U. S. mails)

Specimens are 3½ x 3¾″, *$150.00;* 2½ x 3″, *$65.00;* 2¼ x 3½″, *$60.00;* 2 x 2⅞″, *$50.00;* 2 x 2¼″, *$50.00;* 1¾ x 2½″, *$40.00;* 1½ x 2¼″, *$25.00;* 1 x 1½″, *$20.00;* 1¼ x 2″, *$12.50;* 1 x 1¾″, *$12.00, $10.00;* 1 x 1½″, *$7.50;* 1¼ x 2″, *$6.00, $5.00;* ⅞ x 1″, *$5.00*

A list of the various uranium and thorium minerals in Ward's stock will be mailed free upon request

Crystallized Witherite from Rosiclare, Illinois
A series of specimens of unusual crystallized witherite from this famous fluorite locality has just been received. Specimens consist of attractive groups of stout gray and yellowish white crystals which exhibit the characteristic repeated twinning which simulates hexagonal forms. The crystal faces are deeply striated due to oscillatory growth of prism and pyramid. Specimens fluoresce bluish white under both long and short ultra-violet lamps. Specimens average 2 x 2″ to 2 x 3″, *$3.00, $3.50, $4.00;* 2½ x 3½″, to 3 x 4″, *$5.00, $6.00;* 3½ x 4½″, *$7.50;* 4 x 5½″, *$12.50;* 5 x 7½″, *$17.50*

Chrysoberyl. Custer, South Dakota. Gray tabular xline masses in pegmatite are now available from this new U. S. locality. Specimens average 2 x 2″, *$.50, $.75;* 2 x 3″, *$1.00, $1.50;* 3 x 4″, *$2.00, $2.50, $3.00*

Recent Acquisitions from Sweden

Berzeliite. Långban, Sweden. An arsenate of calcium, sodium, magnesium and manganese, occurring as bright yellow masses in rock. Sizes average 2 x 2″ to 3 x 3″, *$3.50, $4.00;* 3 x 4″ to 3½ x 5″, *$5.00, $6.00, $7.50*

Kentrolite. Långban, Sweden. A lead manganese silicate occurring as black masses in manganophyllite. Specimens average 1 x 2″ to 3 x 3″, *$3.00, $3.50, $4.00, $5.00;* 3 x 4″, *$6.00, $7.50*

All prices are F.O.F. Rochester, N.Y.

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